

AROMA OF HOPS: A STUDY OF THE VOLATILE OIL WITH RELATION TO THE GEOGRAPHICAL SOURCES OF THE HOPS

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At the present time the principal method for distinguishing the kind and source of hops is by means of their appearance and odor. This must necessarily be an uncertain and crude method because of the inability of individuals to differentiate accurately between similar odors, and, hence, it can serve only to determine extremes in the quality of the hops. If, therefore, a scientific method based on the actual properties of the hops could be worked out, it would be considerably more satisfactory and accurate. Since the aroma, which is conceded to be an important factor in judging hops, can be readily concentrated in the volatile oil, it was thought that a systematic comparison of the properties of oils distilled from hops obtained from the various hop-producing countries of the world and grown during different seasons would give information which would be valuable not only as a means for judging the quality but also to determine the geographical source of the hops.

FACTORS WHICH INFLUENCE THE AROMA OF HOPS

Since altitude, light, hygrometric conditions, and the composition of the soil affect the composition of the volatile oils of thyme, lavender, rosemary, and peppermint (Jeancard and Satie, 1909; Bonnier, 1894; Lamothe, 1908; Mossler, 1912)¹, it may be easily seen that hops grown in separated localities under different conditions of climate and soil may be widely different in aroma and may produce volatile oils with distinct and constant variations in their chemical properties. This assumption is practically substantiated by Briant and Meacham (1896), who discuss the influence of climate, ripeness, soil, drying, and general manipulation on the value of hops. The amount of rain and sunshine alters the conditions of ripening, and the different degrees of ripeness have a decided effect upon the quality of the hops. Regarding the influence of soil upon the quality of the product, these authors state:

The effect of soil is, however, undoubtedly very great, for it comes within our experience that on two farms in the same neighborhood but with different soils the hops grown upon one are year after year of a decidedly superior character both as regards resins and flavor, to those on the other, although both are farmed in similar manner and with practically the same climatic conditions.

¹ Bibliographic citations in parentheses refer to "Literature cited," p. 158-159.

According to Sykes and Ling (1907), it is well known that hops grown in different parts of the world differ in aroma. It is further stated that, since the oil from California hops yields the same compounds as the oil from Bavarian or English hops, the difference in odor must be due to the different proportions in which the constituents exist.

While it can not be said with certainty that the aromatic constituents of hops are useful industrially, yet they are of sufficient importance not to be overlooked. Concerning the use of the volatile oil in determining the value of hops, Chapman (1898, p. 233) observes:

It is, in the first place, perhaps, the surest guide to the general value of a sample of hops, when reliance is placed upon a physical examination alone * * *. In the selection of hops * * * the essential oil is certainly the constituent to which chief attention should be paid.

Hops with a fine, agreeable bouquet are usually preferred to those with a poorer odor. If, therefore, differences in odor are clearly perceptible in different hops, a comparison of the volatile oils should be most important in determining possible differences in the aromatic quality of the hops. Since the volatile oil is the carrier of the aroma and since the aroma is a factor in judging hops, it should be possible to compare the aroma of one sample of hops with another by means of the volatile oil from each.

ESTERS AS THE PRINCIPAL ODOR BEARERS

Since esters are important factors in determining the odorous quality of volatile oils, it was thought that perhaps this would be a good point of attack for the comparison of the various hop oils. The very agreeable odor of the oil of hops would indicate the presence of esters, and a preliminary test showed them to be present in considerable quantity.

The ester content is easily measured and may be expressed by the ester number. While this value does not express the exact percentage of any particular ester, yet for comparative purposes it answers equally well. For the purpose, therefore, of making a logical chemical comparison of the several oils, the ester value was adopted as being possibly the constant most likely to show any fluctuation which would have a direct bearing on the aromatic quality.

PHYSICAL AND CHEMICAL PROPERTIES OF OILS AS A BASIS FOR COMPARISON

The physical properties of volatile oils often show variations sufficient to enable comparisons to be made. The specific gravity of most volatile oils is an important factor in their investigation and is influenced to a considerable extent by the source and condition of the plant from which the oil is distilled, as well as by the nature of the constituents of the oil. Optical rotation is a property of volatile oils which is very important,

being dependent almost entirely upon the character of the chemical constituents of the oils. Refraction, although less important than either specific gravity or optical rotation, is of value, since some relationship is known to exist between the chemical compounds and their refractive power. Another physical property which is largely affected by the character of the constituents of the oil is its solubility in alcohol or in dilute alcohol. The presence of terpenes in oils retards solubility, while oxygenated compounds, such as esters and alcohols, increase it.

The boiling points of the various constituents differ considerably. This property is often utilized in the examination of oils for the purpose of effecting a partial separation of the constituents by fractional distillation. The thoroughness of this separation depends largely upon the form of the distilling flask and upon the rapidity of distillation.

All these physical properties were determined for the various samples of hop oils in the hope of detecting any possible differences which might exist.

For further comparison, acidity and saponification values were also determined, although they are of less importance. The determination of alcohols, while important in many oils, was not feasible in this investigation because of the nature of hop oil. It was found that acetylation would not take place quantitatively, and, hence, a measurement of the alcohol content was impossible.

An approximate comparison of the terpene and sesquiterpene content was made possible from the fractionation experiments.

Inasmuch as there is no direct method of assay available which is applicable to oil of hops, it was thought that a careful determination of certain physical and chemical properties of different hop oils would yield data from which a logical comparison could be made. All of the above-mentioned physical and chemical constants are likely to vary with the different conditions of climate, soil, cultivation, ripening, and curing of the hops.

GENERAL PLAN OF COMPARISON OF VARIOUS HOPS AND HOP OILS

In order to learn whether any constant differences exist in the various kinds of hops, it was planned to compare the oils distilled from hops grown in the hop-producing sections of the United States with the oil distilled from an authentic sample of imported hops, all the samples to be from hops grown during the same season. The sections chosen in the United States were California, Oregon, Washington, and New York. The imported hops were from Bohemia.

A comparison of oils obtained from the hops during a single season would give results which would be valuable in determining differences for that particular season, but it was of the most importance to ascertain whether the same differences occurred from year to year. Therefore the experiments were carried on for four successive seasons, and

the oils obtained from the hops of any one locality were compared with those from the same locality during these years. This procedure permitted an absolutely fair comparison by which similarities or differences in the properties of the oils could be easily followed and any fluctuations readily noted.

DISTILLATION OF THE VOLATILE OILS

The usual method of steam distillation was applied for the extraction of the volatile oils from the various samples of hops. The conditions of distillation were practically identical in all cases, each sample being distilled until no more oil was noticeable. From 100 to 200 pounds of California, Oregon, and Washington hops and from 50 to 100 pounds of New York and imported hops were distilled. The California hops were from Perkins, Cosumne, Ukiah, and Wheatland. The Oregon samples were from Independence, the Washington samples from Chehalis, and the New York samples from near Waterville. All were representative samples of commercial, sulphured hops. The imported hops were from Saaz, Bohemia. The distilling apparatus consists of a steel body, steel head, condenser, and receiver.^a The material to be distilled was packed firmly in the still, to which the steel head was then securely clamped, after which steam was passed slowly through the material and the condensed vapors collected in the receiver, the volatile oil separating in a distinct layer on the aqueous distillate.

The yields of oil obtained from the various hops during the four successive seasons are given in Table I.

TABLE I.—Yields of volatile oil from various hops during the years 1906 to 1909, inclusive.

| Source of hops. | Years. | | | | | |
|----------------------------------|----------------------------|------------------|------------------|------------------|------------------|------------------|
| | 1906 (cold storage). | 1906 | 1907 | 1908 | 1909 | Average. |
| California: | <i>Per cent.</i> | <i>Per cent.</i> | <i>Per cent.</i> | <i>Per cent.</i> | <i>Per cent.</i> | <i>Per cent.</i> |
| Perkins No. 1..... | | | 0.20 | 0.38 | 0.43 | 0.336 |
| Cosumne..... | | | .32 | .24 | .42 | .326 |
| Perkins No. 2 ^b | | | | .37 | .33 | .350 |
| Ukiah..... | | | .23 | .53 | .28 | .346 |
| Wheatland..... | | | .21 | .20 | .44 | .283 |
| Oregon..... | 0.30 | 0.34 | .20 | .32 | .30 | .290 |
| New York..... | | .32 | .16 | .14 | .15 | .192 |
| Washington..... | | | | .36 | .38 | .370 |
| Imported (Saaz)..... | .33 | .45 | .32 | .23 | .24 | .310 |

^a A detailed description of the distilling apparatus is given in Bulletin 195 of the Bureau of Plant Industry (Rabak, 1910).

^b Grown at the Brewer ranch, located near Perkins, on the opposite side of the American River.

Considerable variation exists in the yield of oil from the different California hops, not only among the different samples of any one season, but also among the same hops during successive seasons. The average yield of oil from all the California hops during 1907, 1908, and 1909 was 0.32 per cent. Perkins, Cosumne, and Ukiah hops yielded oils which averaged very well during the three seasons. The oil from the Wheatland hops was somewhat below the general average.

The Oregon hops which were distilled during the four successive years showed an average oil content of 0.29 per cent, which is a trifle less than the average California sample.

The New York hops, with an average during the four years of 0.192 per cent of oil, were noticeably lower in oil content than any of the other hops distilled. Only in one year, 1906, did the yield approach that of the California, Oregon, Washington, or the imported hops.

The Washington hops, which were distilled only during two seasons, appear to possess the highest percentage of oil, the average being 0.37 per cent.

The imported hops distilled from the crops of 1906, 1907, 1908, and 1909 showed an average yield of 0.31 per cent of oil, considerable change appearing from season to season.

When distilled for a period of more than two seasons, all the hops showed considerable fluctuation in the yield of oil. Named in the order of their average yield the hops group themselves as follows: Washington, California, imported (Saaz), Oregon, and New York.

This variability in the oil content may be ascribed to varying conditions of climate and soil, as well as to ripeness and drying of the hops, which would affect the formation of the oil in the plant. Slight differences in yield of oil would not necessarily influence the quality, since the same proportion of odoriferous constituents may still be present.

PHYSICAL PROPERTIES OF THE VARIOUS OILS

The physical properties of the oils permit a somewhat better means for comparison, and therefore a record was made of the color, odor, and taste of each of the oils mentioned. Differences in color are, of course, readily noted, but differences in odor and taste are considerably less noticeable, because of the difficulty with which the senses of smell and taste distinguish closely related substances. The specific gravity, refractive power, and solubility, each of which can be accurately measured, are of much greater importance, although even these properties are usually entirely inadequate for detecting constant differences. However, as they are affected by the constituents of the oils they are sometimes of considerable value. In all cases the oils were too dark to permit making determinations of the optical rotation, which is often useful in detecting certain differences in composition. The tabulation shows the physical properties of the various hop oils distilled during the seasons 1907, 1908, and 1909 (Table II).

TABLE II.—*Physical properties of various hop oils distilled during several successive seasons.***COLOR.**

| Source of hops. | 1907 crop. | 1908 crop. | 1909 crop. |
|----------------------|-------------------------|--------------------------|---------------------|
| California: | | | |
| Perkins No. 1..... | Brownish red..... | Dark brownish red..... | Light brownish red. |
| Cosumne..... | Light brownish red..... | do..... | Dark brownish red. |
| Perkins No. 2..... | | Pale brown..... | Wine red. |
| Ukiah..... | Dark brownish red..... | Reddish brown..... | Do. |
| Wheatland..... | Pale brown..... | do..... | Reddish brown. |
| Oregon..... | Wine red..... | do..... | Dark reddish brown. |
| New York..... | Deep brownish red..... | Bright brownish red..... | Deep brownish red. |
| Washington..... | | Light brownish red..... | Light wine red. |
| Imported (Saaz)..... | Brown..... | Brownish red..... | Dark brown. |

ODOR.

| | | | |
|----------------------|---|--|------------------------------------|
| California: | | | |
| Perkins No. 1..... | Strongly aromatic, characteristic. | Strongly aromatic, musty, not agreeable. | Strongly aromatic, not unpleasant. |
| Cosumne..... | Agreeable, hop-like, very aromatic. | Pleasant, aromatic, hop-like. | Strongly aromatic, agreeable. |
| Perkins No. 2..... | | Slightly musty, sour, strongly aromatic. | Very pleasant, flowery. |
| Ukiah..... | Strongly aromatic..... | Strongly aromatic..... | Slightly fatty, aromatic. |
| Wheatland..... | Strongly aromatic, disagreeable. | Strongly aromatic, pleasant, characteristic. | Strongly aromatic, not agreeable. |
| Oregon..... | Extremely strong aromatic, not agreeable. | Strongly aromatic, slightly musty. | Strongly aromatic, pleasant. |
| New York..... | Strong, characteristic, not agreeable. | Musty and unpleasant, aromatic. | Strongly aromatic, not agreeable. |
| Washington..... | | Agreeable and strongly aromatic. | Agreeable and aromatic. |
| Imported (Saaz)..... | Mild, aromatic, agreeable. | Very pleasant, characteristic. | Pleasant, mild, characteristic. |

TASTE.

| | | | |
|----------------------|---|--|---|
| California: | | | |
| Perkins No. 1..... | Slightly fatty, slightly pungent. | Slightly pungent, slightly bitter. | Slightly pungent, slightly bitter. |
| Cosumne..... | Aromatic, not pungent, slightly bitter. | Fatty, slightly bitter, aromatic. | Fatty, bitter, pungent. |
| Perkins No. 2..... | | Slightly fatty, aromatic, faintly pungent. | Slightly fatty, bitter, faintly pungent. |
| Ukiah..... | Bitter, slightly pungent, aromatic. | Fatty, slightly pungent, aromatic. | Fatty, becoming aromatic and bitter. |
| Wheatland..... | Bitter, aromatic, slightly pungent. | Bitter, aromatic, slightly pungent. | Fatty, slightly bitter, pungent. |
| Oregon..... | Slightly pungent, becoming slightly bitter. | Fatty, becoming slightly bitter. | Slightly fatty, slightly bitter. |
| New York..... | Bitter, aromatic, not pungent. | Slightly fatty and bitter, slightly pungent. | Slightly sour, slightly bitter and pungent. |
| Washington..... | | Slightly fatty and bitter, very little pungency. | Slightly bitter, slightly pungent. |
| Imported (Saaz)..... | Fatty, slightly bitter, not pungent. | Fatty, aromatic, slightly pungent. | Fatty, aromatic, very slightly pungent. |

TABLE II.—Physical properties of various hop oils distilled during several successive seasons—Continued.

SPECIFIC GRAVITY AND INDEX OF REFRACTION.

| Source of hops. | Specific gravity, 20° C. | | | Index of refraction at 20° C. | | |
|-----------------------|--------------------------|------------|------------|-------------------------------|------------|------------|
| | 1907 crop. | 1908 crop. | 1909 crop. | 1907 crop. | 1908 crop. | 1909 crop. |
| California: | | | | | | |
| Perkins No. 1. | 0.821 | 0.838 | 0.8316 | 1.4838 | 1.4783 | 1.4716 |
| Cosumne. | .821 | a. 8395 | .842 | 1.4825 | 1.4724 | 1.4733 |
| Perkins No. 2. | | a. 8289 | .8422 | | 1.4691 | 1.4743 |
| Ukiah. | .821 | a. 831 | a. 839 | 1.4890 | 1.4737 | 1.4718 |
| Wheatland. | .828 | .8443 | .8358 | 1.4870 | 1.4753 | 1.4743 |
| Oregon. | .8343 | .838 | .8433 | 1.4802 | 1.4730 | 1.4705 |
| New York. | b. 859 | b. 834 | b. 8747 | 1.4804 | 1.4756 | 1.4800 |
| Washington. | | .850 | .8464 | | 1.4763 | 1.4734 |
| Imported (Saaz). | b. 852 | b. 821 | b. 858 | 1.4905 | 1.4852 | 1.4829 |

^a Specific gravity at 23° C.^b Specific gravity at 24° C.SOLUBILITY.^a

[Quantity of oil dissolved in 3 volumes of 94 per cent alcohol.]

| Source of hops. | 1907 crop. | 1908 crop. | 1909 crop. |
|--------------------|---|---|--|
| California: | | | |
| Perkins No. 1. . | 0.55 volume oil, turbid, yellowish residue. | 0.7 volume oil, turbid. | 0.8 volume oil. |
| Cosumne. | 0.5 volume oil, whitish residue. | 0.85 volume oil, brownish residue. | Do. |
| Perkins No. 2. . | | 0.7 volume oil, turbid. | 0.75 volume oil, slightly turbid. |
| Ukiah. | 0.35 volume oil, slight turbidity, yellowish-brown residue. | 0.85 volume oil, turbid. | 0.95 volume oil, slightly turbid, with reddish residue. |
| Wheatland. | 0.35 volume oil, turbid, yellowish residue. | 0.75 volume oil, brown residue. | 0.7 volume oil. |
| Oregon. | 0.65 volume oil, turbid, yellow residue. | 0.9 volume oil. | 1 volume oil. |
| New York. | 0.85 volume oil, brown residue. | 0.85 volume oil. | 0.8 volume oil, light brown. |
| Washington. | | 0.85 volume oil, turbid. | 0.9 volume oil. |
| Imported (Saaz). . | 0.75 volume oil, slightly turbid. | 0.5 volume oil, yellow viscous residue. | 0.75 volume oil, slightly turbid, bark-brown, viscous residue. |

^a Solubility of 1907 crop determined after two years; 1908 crop determined after one year.

Color, odor, and taste, which appeal solely to the senses, are not especially significant. The colors of the various oils, ranging from a golden yellow to a dark brown, were due largely to the condition of the material and the time of the distillation. The first runnings obtained in all of the distillations were nearly colorless, but gradually deepened in color as the distillation progressed. The predominant colors seemed to be red and brown, the golden-yellow color being obtained only when small quantities of hops were distilled on a small laboratory scale. Whenever large quantities (100 to 200 pounds) were distilled, the resulting oil invariably possessed a dark color, the particular tint varying with the season. No constant difference was observed in oils from the various sources.

The odor in all cases was naturally characteristic of hops. In some instances, however, a slightly musty odor was perceptible. The oils from the American hops were all strongly aromatic and in most cases agreeable. A slight yet distinctly musty odor was perceived in several of the oils, due probably to imperfect drying and subsequent sweating of the hops in the bale. The oils from the foreign hops seemed to be distinctly different from the American oils, possessing a very pronounced flowery odor, combined with a fatty odor, the effect being most agreeable.

The sense of taste, which is influenced directly by the sense of smell, is generally capable of distinguishing definite and characteristic qualities of a substance, such as pungency and bitterness. Acidity and fattiness can also be easily detected. All of the oils in question had a decidedly aromatic taste, and there were also a number in which bitterness, fattiness, and acidity were very pronounced. The oils from the California hops were all characterized by bitterness and pungency, with slight fattiness. The oils from the imported hops were strongly fatty with only very slight bitterness and pungency.

The densities of the California oils bore a close relationship during individual seasons, differing somewhat from season to season. This would seem to indicate that the approximate composition during any one season was about the same in the several oils. The average specific gravity of the several California oils for the three seasons was about 0.8326. It will be seen that the Oregon oils were somewhat higher, the average being 0.8385. The oils from the imported hops, with an average specific gravity of 0.8433, and the Washington oils, with an average of 0.8482, followed in order. The oils with the highest general specific gravity were those from the New York hops, which averaged 0.8554 at 24° C. This figure would be increased if corrected to the temperature at which the specific gravity of the majority of the oils was recorded. It is generally acknowledged that the specific gravity is modified by the composition of an oil, but it is doubtful whether the differences noted above would cause any remarkable change in the quality of the oil. A

high specific gravity would usually be accompanied by a larger percentage of high-boiling constituents, and vice versa.

From Table II it is readily seen that the refraction of the California oils during each of the three years shows but little variation. During the successive seasons the refraction of the oils from the 1907 crop was somewhat higher than that of the two following years. This was accounted for by the fact that the index of refraction of the oils of the 1907 crop was taken about two years later (1909), showing that a change had taken place in the oils. The refractive property of the Oregon, New York, and Washington oils, as compared with the California oils, was not greatly different. However, the oils from the imported hops showed a higher refractive index than any of the other oils. This, again, may be due to the presence of a somewhat higher percentage of highly refractive constituents in these oils.

The solubility of a volatile oil in alcohol depends upon the composition of the oil. A high percentage of terpenes and sesquiterpenes decreases the solubility and a high content of oxygenated compounds increases it. Owing to the insolubility of hops oils in alcohol and the difficulty thereby encountered in obtaining comparative results, a deviation was made from the usual method employed for determining solubility. One volume of the oil was thoroughly shaken with three volumes of 94 per cent alcohol in a graduated cylinder, after which the resinous insoluble matter was centrifuged. The amount of insoluble matter could then be easily read on the bottom of the cylinder and the percentage of dissolved material readily calculated.

Apparently the most soluble oil among the number was the oil from the Oregon hops, one volume of oil from the 1909 crop dissolving completely in three volumes of 94 per cent alcohol, the oil from the 1908 crop being almost as soluble. Washington and New York oils from the crops of 1908 and 1909 were slightly less soluble than the Oregon oils. The California oils of these two seasons were a trifle less soluble than those from the Washington and New York hops, while the imported oils appeared to be the least soluble.

The much lower solubility of the 1907 oils was due to the fact that the determinations were not made until two years after distillation. Although the oils had been kept in well-filled bottles and well protected from the light, decomposition had ensued, which resulted in the formation of less soluble constituents, thus decreasing the solubility of the oils. This plainly shows the effect of age on the solubility of the oils.

From the information thus obtained it would appear that the oils with the highest solubility probably contained a larger percentage of oxygenated compounds and a lower percentage of terpenic compounds than the less soluble oils.

CHEMICAL PROPERTIES OF THE VARIOUS OILS

In order to make a better comparison of the several oils with regard to their aromatic quality, determinations were made of the acid, ester, and saponification numbers. These constants are usually ascertained in order to get some idea of the odoriferous constituents.

The determination of the acid number is readily accomplished by simple titration with standard alkali and is expressed by the number of milligrams of potassium hydroxid required to neutralize the free acidity contained in 1 gram of the oil. A number of factors may tend to influence this value. Freshly distilled oils, in most instances, are low in free acidity, while old oils or oils distilled from old material usually possess a larger quantity of free acids. Improper conditions of drying and storing have a tendency to cause changes to take place in the aromatic compounds, which result in the formation of free acids, and thereby increase the acid numbers.

As previously stated, the esters, which consist of combinations of acids and alcohols, are considered the odor bearers. These values are easily determined by saponifying the oil with alcoholic alkali and calculating the number of milligrams of potassium hydroxid consumed in the reaction by 1 gram of oil. This represents an accurate measurement of the ester constituents. As in the case of free acidity, this value may also be affected by conditions under which the material is dried and stored. The stage of growth and development of the plant is also a strong factor in modifying the ester content of volatile oils.

The saponification number represents the total amount of alkali, expressed in milligrams, necessary to react completely with 1 gram of oil, being the sum of the acid and ester numbers.

These constants which are so directly related to the odor were carefully determined for each of the hop oils distilled from the various samples of hops. A determination of the free alcohols in these oils was also made, but was barren of results in all cases. Acetylation with acetic-acid anhydrid with subsequent saponification is necessary and is readily accomplished in many oils. However, the nature of some alcohols is such that a quantitative acetylation is impossible, owing to decomposition when boiled with the acetic-acid anhydrid. Modification of the usual method, altering the length of boiling and the quantity of acetic anhydrid, gave negative results in all cases. From this peculiar behavior of the oil it is inferred that either the oils have no free alcohol compounds or that the alcohol compounds, if present, are of such a nature as to be incapable of quantitative acetylation.

The acid, ester, and saponification numbers of the oils from the American and foreign hops are recorded in Table III.

TABLE III.—The acid, ester, and saponification numbers of hop oils distilled during several seasons.

| Sources of hops. | Acid numbers. | | | | | | Ester numbers. | | | | | | Saponification numbers. | | | | | |
|----------------------|---------------|------|------|------|------|----------|----------------|------|------|------|------|----------|-------------------------|------|------|------|------|----------|
| | 1906 | 1907 | 1908 | 1909 | 1910 | Average. | 1906 | 1907 | 1908 | 1909 | 1910 | Average. | 1906 | 1907 | 1908 | 1909 | 1910 | Average. |
| California: | | | | | | | | | | | | | | | | | | |
| Perkins No. 1..... | 0.0 | 1.5 | 1.1 | 0.86 | 42.0 | 47.0 | 47.1 | 45.5 | 42.0 | 48.5 | 48.2 | 46.2 | | | | | | |
| Cosumne..... | 0 | 2.4 | 2.9 | 1.76 | 45.0 | 46.0 | 51.0 | 47.3 | 45.0 | 48.4 | 53.9 | 49.1 | | | | | | |
| Perkins No. 2..... | | 1.6 | 2.0 | 1.80 | 45.0 | 43.7 | 44.3 | 46.6 | 45.7 | 46.1 | | | | | | | | |
| Ukiah..... | 0 | 1.1 | 1.8 | 0.96 | 40.8 | 44.0 | 51.0 | 45.2 | 40.8 | 45.1 | 52.8 | 46.2 | | | | | | |
| Wheatland..... | 2.3 | 2.0 | 1.4 | 1.90 | 50.0 | 45.5 | 41.0 | 45.5 | 52.3 | 47.5 | 42.4 | 47.4 | | | | | | |
| Oregon..... | 5.5 | 1.6 | 1.0 | 2.8 | 2.70 | 72.0 | 57.0 | 50.2 | 56.0 | 58.8 | 77.5 | 58.6 | 51.2 | 58.8 | 61.5 | | | |
| New York..... | 4.8 | 3.6 | 2.1 | 2.5 | 44.0 | 61.0 | 47.0 | 51.8 | 50.9 | 48.8 | 64.6 | 49.1 | 54.3 | 54.0 | | | | |
| Washington..... | | 1.0 | 1.5 | 1.25 | 51.8 | 53.8 | 52.8 | 52.8 | 52.8 | 55.3 | 54.0 | | | | | | | |
| Imported (Saaz)..... | 1.5 | 1.5 | 1.0 | 3.0 | 3.1 | 2.02 | 12.6 | 20.0 | 36.0 | 28.6 | 20.4 | 23.5 | 14.1 | 21.5 | 37.0 | 31.6 | 23.5 | 21.0 |

The oils, in the order of their average acidity, were as follows: New York, Oregon, imported, California, and Washington. In every instance the New York oils showed comparatively high acidity. Whether this high acidity content was inherent in the oil or whether it was due to conditions of drying and storing can not be stated. The high acidity seemed to be general, since two other samples of New York hops (not recorded) yielded oils with the acid numbers 2.6 and 3.2, respectively. The average acidity of the Oregon hop oil as given is probably somewhat high, as it was considerably augmented by the high acid number of the oil from the 1906 crop, which was distilled from a sample of hops that were not in as fresh condition as the 1907, 1908, and 1909 hops. The oils from the imported hops were somewhat lower than those from the Oregon hops, being fairly constant in 1906, 1907, and 1908, but much higher in 1909 and 1910. These were followed by the California and Washington oils, with an average of 1.41 and 1.25, respectively.

The high and low acid numbers were significant of nothing important as far as the aroma was concerned, as the free acidity did not perceptibly affect the odor of the oil.

The ester numbers revealed most striking similarities and dissimilarities, not only during one season but for several successive seasons. It was to be expected that the oils from the hops during any one season would show differences, but that these same differences should appear during three, four, and even five successive seasons was most surprising.

The oils from the imported hops were conspicuous because of the fact that the data for the several seasons showed the ester content to be only about one-half as great as the ester content of the oils from the California, Oregon, Washington, and New York hops. Besides the samples recorded in the table, a cold-storage sample of Saaz hops of the 1906 crop, distilled one year later, gave an oil with an ester number of

24. Three samples of Dauber, Auscher, and Oesterreich Gewächs hops of the 1910 crop possessed the ester numbers 15.7, 21.3, and 18, respectively. Figure 1 shows that the nine samples of foreign oils were uniformly lower in esters than the American oils.

The close relationship of the ester numbers of the California oils during the seasons of 1907, 1908, and 1909 is very evident. The general average ester number of the California oils was 45.5, as compared with 50.9 for New York, 52.8 for Washington, 58.8 for Oregon, and 23.5 for the imported. No important difference was noted in the various California oils. This is true also of the Washington oils, which, however, were distilled during only two seasons. The ester content of the Oregon oils averaged considerably higher than the oils from any of the other hops and, with the exception of the oil from the 1906 crop, the history of which was doubtful, the oils bear close relationship from year to year. The New York oils were slightly more variable, but nevertheless occupy about the same relative position from year to year with respect to the other oils.

In the case of the foreign oils, the ester numbers, which are a measure of the odorous constituents, would seem to point to a consistently lower content of these compounds. That this unusually low ester content is responsible for the generally acknowledged superior aroma of imported hops can not be positively stated, although it is highly probable, since it is known that other oils with a low ester content, notably lavender and peppermint oils, are more agreeable and fragrant than oils with a high ester content.

The saponification numbers, which represent the total acids and esters in the oils, presented practically the same constant differences and similarities brought out by comparison of the ester numbers.

While it is not known whether the ester numbers would continue lower indefinitely in case of the foreign oils, it may be assumed that such would probably be the case, since the authentic samples distilled during the five seasons showed abnormally low values as compared with the American oils. In like manner, it may also be assumed that the high ester numbers of the American oils would continue indefinitely, since they were fairly constant during the three seasons in which the experiments were carried on.

FRACTIONATION OF THE VARIOUS OILS

Since volatile oils are composed of a number of constituents with boiling points which often vary considerably, fractional distillation has proved a useful and effective method for the partial separation of these constituents. Ordinarily a straight-neck distilling flask with side tube is used for this purpose, the bulb of the thermometer being placed immediately opposite the mouth of the tube and the fractions collected at different intervals. By this means a partial separation of the con-

stituents is accomplished. A better separation, however, can be made by means of a 3-bulb Ladenburg distilling flask, which is a flask with

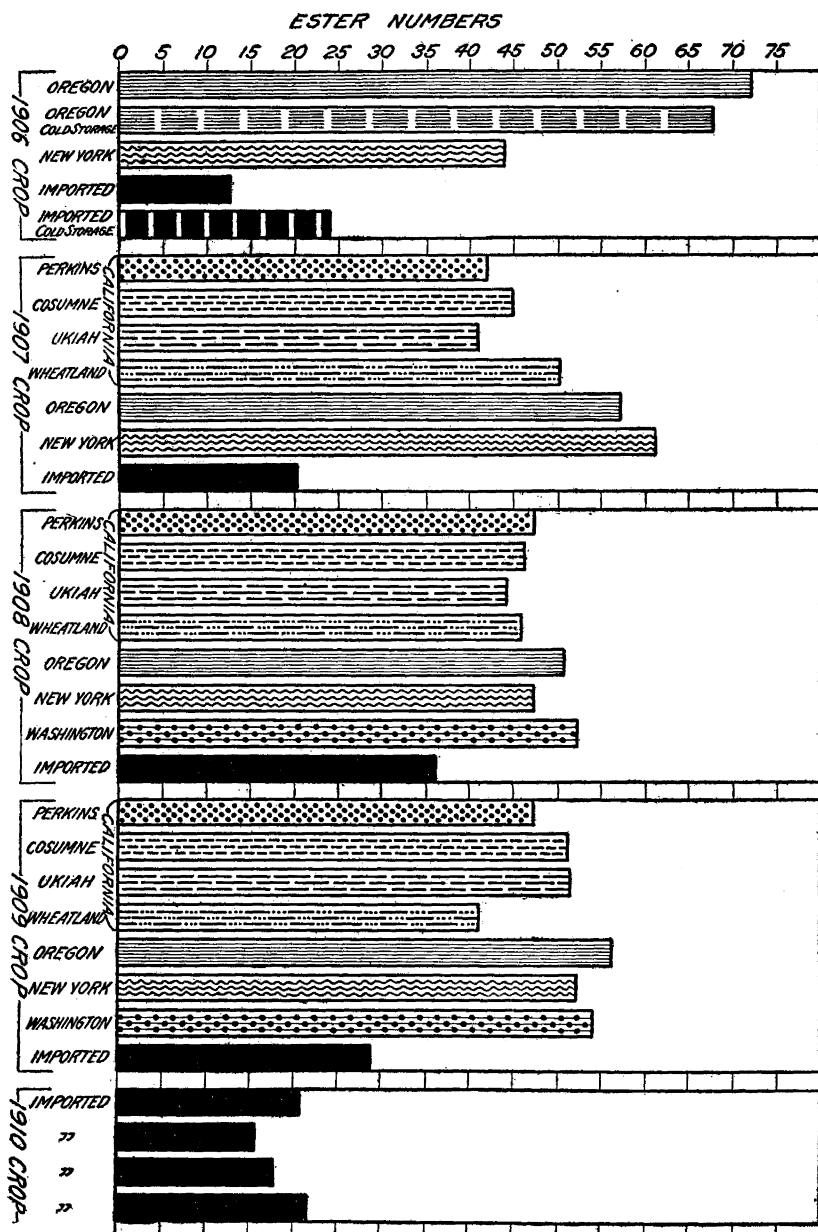


FIG. 1.—Relative ester content of various hop oils.

three bulbs blown in the neck below the side tube and the flask proper. These bulbs act like a distilling column, causing a more complete sepa-

ration of each of the constituents of the oil. In the fractionation of the various hop oils, a flask of this sort having a capacity of 200 cubic centimeters was employed. The bulb of the thermometer was placed directly opposite the outlet tube in all the experiments. The rapidity of distillation was also regulated so that about the same amount of oil distilled during a given period of time. Fractions were collected between different temperatures, the same range of temperature being maintained in the distillation of each oil. Even with all these precautions it was impossible to make the separation of the compounds entirely complete. Vacuum distillation would possibly have effected the separation with less decomposition, but the difficulty of keeping conditions alike in each case would hardly compensate for the partial decomposition which is unavoidable by direct distillation. With the conditions of distillation practically alike in each fractionation, approximately the same amount of decomposition should result in the high-boiling fractions in each oil.

For purposes of comparison, fractionation by direct distillation was employed with each sample of oil from the various kinds of hops, seven fractions being collected from the oil of the 1906 crop, as follows: Fraction 1, 165° to 185° C.; fraction 2, 185° to 205° C.; fraction 3, 205° to 225° C.; fraction 4, 225° to 245° C.; fraction 5, 245° to 260° C.; fraction 6, 260° to 275° C.; fraction 7, 275° to 290° C.; and finally the residue 290° C. +. Seven fractions were also collected from the oils of the 1907, 1908, and 1909 crops between somewhat different temperatures, as will be seen in the tables. The percentage of oil distilled was calculated for each fraction of the various oils of the crops of 1906, 1907, 1908, and 1909.

In order to facilitate comparisons and to bring out more forcibly the differences in the approximate composition of the oils, as manifested by the fractionation, tabulations were made of the oils distilled each season. The figures in Table IV express the percentage of oil distilled at the temperatures indicated. Curves were also made of each fractionation in order that the comparison could be seen at a glance (see figs. 2, 3, 4, and 5).

TABLE IV.—*Fractionation of hop oils, showing the percentage distilled at different temperatures for the years 1906 to 1909, inclusive.*

| 1906 CROP. | | | | | | | | |
|------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------------|-----------------------|
| Source of hops. | Fraction 1, 165° to 185° C. | Fraction 2, 185° to 205° C. | Fraction 3, 205° to 225° C. | Fraction 4, 225° to 245° C. | Fraction 5, 245° to 260° C. | Fraction 6, 260° to 275° C. | Fraction 7, 275° C. + | Residue, 290° C. + |
| Oregon..... | 26.9 | 13.1 | 11.55 | 14.7 | 9.2 | 10.3 | 14.25 | |
| Do. ^a | 33.5 | 11.4 | 6.4 | 5.7 | 7.9 | 6.4 | 12.4 | 16.0 |
| New York... | 24.5 | 17.5 | 2.5 | 3.5 | 15.2 | 19.2 | 17.6 | |
| Imported | | | | | | | | |
| (Saaz)... | 9.0 | 9.1 | 2.5 | 8.4 | 25.6 | 27.8 | 17.6 | |
| Do. ^a | 10.0 | 9.2 | 8.5 | 10.0 | 30.0 | 18.6 | 5.7 | 8.0 |

^a In cold storage one year before distillation of the oil.

TABLE IV.—Fractionation of hop oils, showing the percentage distilled at different temperatures for the years 1906 to 1909, inclusive—Continued.

1907 CROP.

| Source of hops. | Fraction 1, 165° C. | Fraction 2, 165° C. to 170° C. | Fraction 3, 170° C. to 185° C. | Fraction 4, 185° C. to 225° C. | Fraction 5, 225° C. to 260° C. | Fraction 6, 260° C. to 275° C. | Fraction 7, 275° C. to 290° C. | Resi- due, 290° C. |
|----------------------|------------------------|---|---|---|---|---|---|--------------------------|
| California: | | | | | | | | |
| Perkins..... | 18.7 | 26.5 | 18.7 | 7.5 | 5.0 | 5.0 | 10.6 | 8.1 |
| Cosumne..... | 24.3 | 15.0 | 14.3 | 5.0 | 3.1 | 7.5 | 14.3 | 16.5 |
| Ukiah..... | 22.0 | 29.0 | 9.0 | 6.7 | 4.0 | 3.2 | 11.5 | 14.6 |
| Wheatland..... | 19.0 | 16.0 | 18.5 | 12.0 | 11.0 | 6.0 | 9.0 | 8.5 |
| Oregon..... | 5.5 | 14.0 | 25.0 | 14.5 | 13.0 | 6.5 | 9.5 | 12.0 |
| New York..... | .0 | 5.7 | 15.7 | 18.8 | 22.8 | 11.0 | 12.8 | 13.2 |
| Imported (Saaz)..... | .0 | 1.7 | 10.0 | 20.5 | 30.0 | 9.1 | 10.7 | 18.0 |

1908 CROP.

| | | | | | | | | |
|----------------------|-----|------|------|------|------|------|------|------|
| California: | | | | | | | | |
| Perkins..... | 3.5 | 6.5 | 25.0 | 14.5 | 13.0 | 4.5 | 14.5 | 18.5 |
| Cosumne..... | 6.5 | 11.5 | 32.0 | 18.0 | 11.6 | 6.0 | 8.0 | 15.8 |
| Ukiah..... | 6.0 | 16.3 | 23.6 | 14.8 | 7.2 | 8.0 | 8.3 | 15.8 |
| Wheatland..... | 4.0 | 11.7 | 27.4 | 17.4 | 12.5 | 9.3 | 8.7 | 9.0 |
| Oregon..... | 7.0 | 7.7 | 23.0 | 20.0 | 17.0 | 8.8 | 6.0 | 8.0 |
| New York..... | 3.1 | 15.3 | 25.3 | 18.8 | 16.6 | 6.8 | 6.0 | 8.0 |
| Washington..... | 3.5 | 4.0 | 12.7 | 20.0 | 18.0 | 13.3 | 11.5 | 17.0 |
| Imported (Saaz)..... | 4.9 | 13.3 | 24.4 | 15.3 | 7.7 | 5.3 | 10.7 | 18.1 |

1909 CROP.

| | | | | | | | | |
|----------------------|-----|------|------|------|------|------|------|------|
| California: | | | | | | | | |
| Perkins..... | 2.5 | 7.0 | 15.0 | 10.0 | 7.5 | 15.4 | 23.4 | 19.2 |
| Cosumne..... | 5.4 | 4.3 | 9.1 | 12.5 | 13.0 | 14.6 | 21.2 | 19.9 |
| Ukiah..... | 3.5 | 11.5 | 21.5 | 20.0 | 12.0 | 7.5 | 12.0 | 12.0 |
| Wheatland..... | 4.1 | 5.8 | 20.8 | 15.4 | 6.6 | 5.4 | 20.0 | 21.9 |
| Oregon..... | 4.1 | 8.3 | 20.8 | 21.4 | 15.8 | 9.1 | 7.5 | 13.0 |
| New York..... | 5.0 | 6.5 | 11.0 | 8.5 | 18.0 | 11.9 | 13.1 | 26.0 |
| Washington..... | 3.7 | 7.2 | 19.0 | 21.5 | 16.5 | 8.8 | 10.6 | 12.7 |
| Imported (Saaz)..... | 4.2 | 5.4 | 10.6 | 25.0 | 13.2 | 15.2 | 26.4 | |

COMPARISON OF FRACTIONATED OILS

As shown by Table IV and figure 2, the fractionation of the oils from the Oregon cold storage and Oregon and New York hops follow entirely different lines from the imported and the cold-storage imported hops. In case of the first three, fraction 1 (165° to 185° C.) represents the major portion of the oil, while the oils from the imported hops are directly the reverse, fractions 5 (245° to 260° C.) and 6 (260° to 275° C.) representing more than one-half of the oils. These results indicate that the oils from

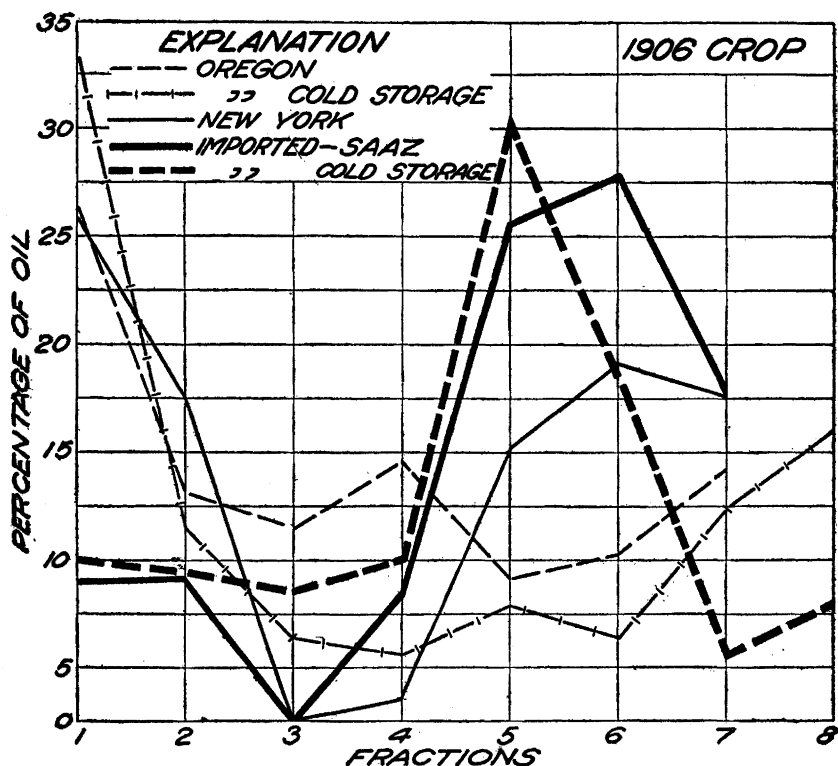


FIG. 2.—Fractionation curves of hop oils from the crops of 1906.

the American hops of the 1906 crop are richest in the low-boiling constituents and the imported oils from the same year are richest in the high-boiling constituents.

The fractionation of the oils of the 1907 crops, as shown also in Table IV and in figure 3, bears out practically the same conclusions. Fractions 1, 2, and 3 (-165° , 165° to 170° , and 170° to 185° C.) of the California oils comprise from 53 to 63 per cent of the original oils, and of the Oregon oil nearly 45 per cent, while the same three fractions of the New York oil correspond to 21 per cent of the original oil. The portion of the imported

oil distilling below 185° C. was only 11.7 per cent of the oil. These results again show the deficiency of the imported oil in the low-boiling constituents. When fractions 4 (185° to 225° C.) and 5 (225° to 260° C.) are considered the reverse conditions exist, these fractions of the imported oils representing about 50 per cent of the oil, 41 per cent of the New York oil, 27 per cent of the Oregon oil, and an average of 13 per cent of the California oils. The curves of the remaining fractions are very similar. The figure shows that the imported oil follows almost a directly reverse course from that of the California and Oregon oils. In this respect the New York oil seems to be the most closely related to the foreign oil.

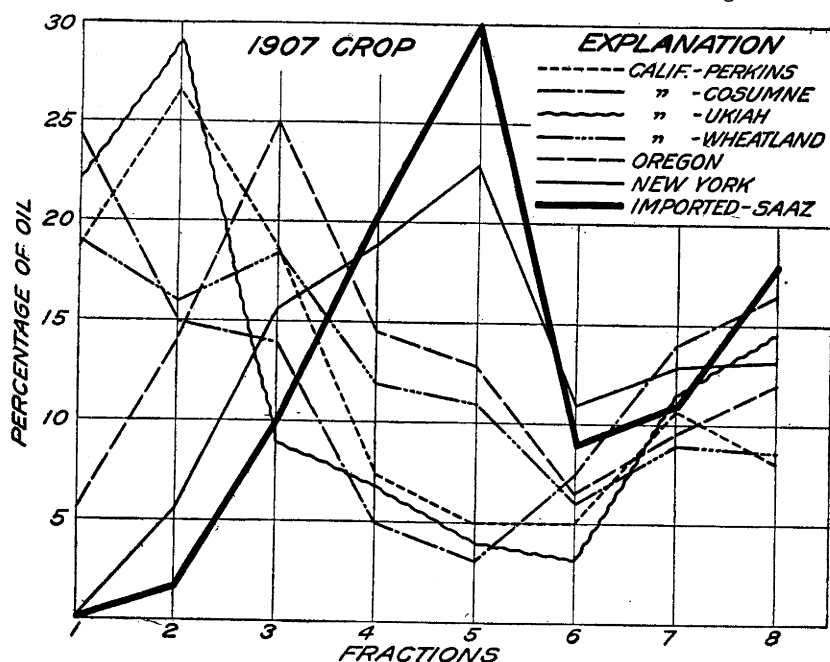


FIG. 3.—Fractionation curves of hop oils from the crops of 1907.

Comparing the various oils of the 1908 crop, as given in Table IV and the curves in figure 4, it will be seen that nearly all show a similar trend in their fractionation properties. The California oils, on an average, again surpass the other oils in constituents which boil below 185° C., the lowest in this respect being those from Washington and Oregon. In that year, for the first time in the three seasons, the fractionation curve of the imported oil followed lines somewhat similar to those of the American oils. No explanation is ventured for this change in the imported oil.

The difference between the imported oil and the other oils of the 1909 crops is also very noticeable in Table IV and figure 5. The California oils of the 1909 crop, as in 1906, 1907, and 1908, distilled over largely in the

first four fractions, the Cosumne oil showing slight deviation. The curve of the first four fractions of the imported oil is again far below that of any of the other oils. From fraction 4 the New York oil follows a similar course to that of the imported oil. Fraction 5 (225° to 260° C.), in both the imported and the New York oils, shows the highest percentage. The similarity of the Oregon and Washington oils is noteworthy, both curves following almost identical lines.

As a general thing, it will be observed that the oils from the California, Oregon, and Washington hops during the several seasons showed a high

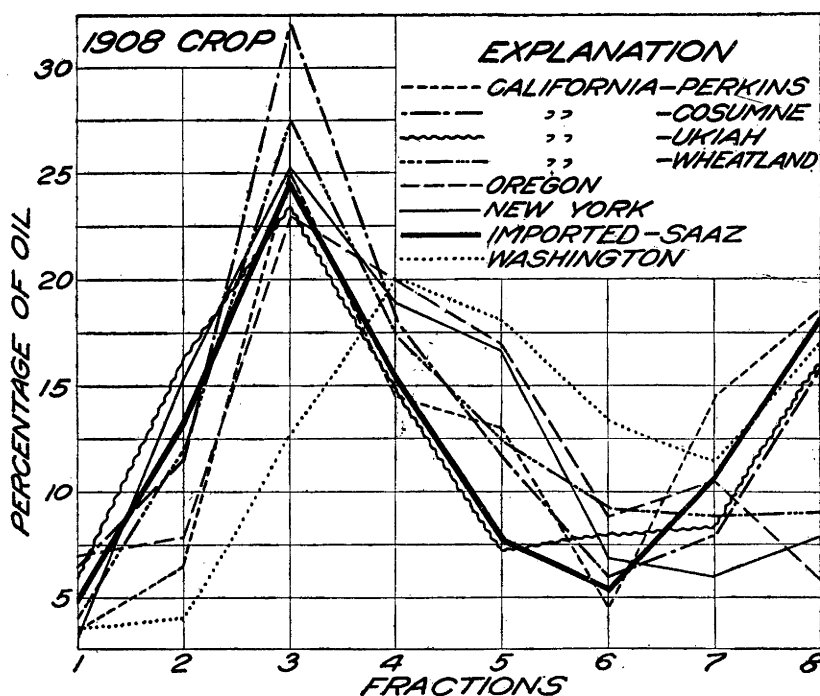


FIG. 4.—Fractionation curves of hop oils from the crops of 1908.

content of low-boiling constituents, while the oils from the imported hops were invariably poorer in the low-boiling constituents. On the other hand, the oils from the imported hops seemed, generally speaking, to contain much higher percentages of the high-boiling compounds, as shown by fractions 4 and 5; the oil of the 1908 crop, however, was unique in that it appeared to be similar to the other oils during that particular season. The curves of the imported oils followed those of the New York oils the most closely, the general direction being similar. The California oils also followed very similar directions, as did the Oregon and Washington oils.

PHYSICAL PROPERTIES OF THE FRACTIONS

SPECIFIC GRAVITY

Although the specific gravity, as a rule, is apt to show only slight differences, owing to the variable composition of the oil, it was thought that determinations of this property might be of some value. The specific gravity of the various fractions from the oils of the crops of 1906, 1907, 1908, and 1909 is given in Table V.

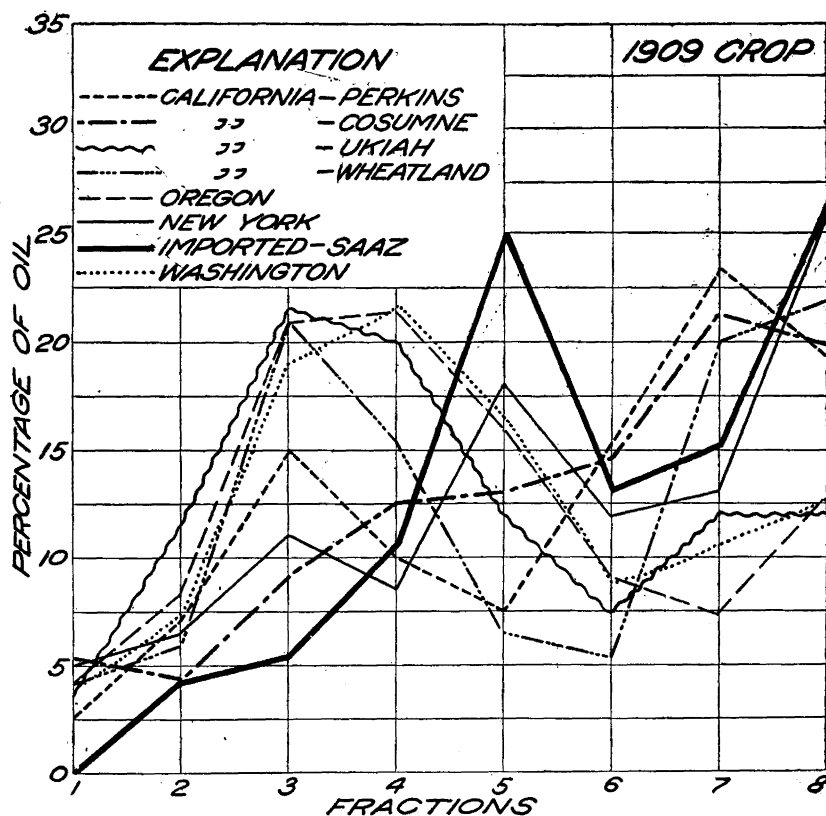


FIG. 5.—Fractionation curves of hop oils from the crops of 1909.

TABLE V.—Specific gravity of fractions of hop oils for the years 1906 to 1909, inclusive.

1906 CROP (AT 25° C.).

| Source of hops. | Fraction 1, 165° to 185° C. | Fraction 2, 185° to 205° C. | Fraction 3, 205° to 225° C. | Fraction 4, 225° to 245° C. | Fraction 5, 245° to 260° C. | Fraction 6, 260° to 275° C. | Fraction 7, 275° C. |
|------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------|
| Oregon..... | 0.818 | 0.821 | 0.849 | 0.876 | 0.877 | 0.881 | |
| Do. ^a | .820 | .839 | .859 | .882 | .894 | .900 | 0.887 |
| New York..... | .813 | .829 | .853 | .862 | .890 | .894 | |
| Imported..... | .815 | .819 | .825 | .835 | .888 | .888 | |
| Do. ^a | .826 | .838 | .850 | .873 | .891 | .896 | .836 |

^a In cold storage one year before distillation.

TABLE V.—*Specific gravity of fractions of hop oils for the years 1906 to 1909, inclusive—Continued.*

1907 CROP (AT 25° C.).

| Source of hops. | Fraction 1, —165° C. | Fraction 2, 165° C. to 170° C. | Fraction 3, 170° C. to 185° C. | Fraction 4, 185° C. to 225° C. | Fraction 5, 225° C. to 260° C. | Fraction 6, 260° C. to 275° C. | Fraction 7, 275° C. to 290° C. |
|----------------------|-------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| California: | | | | | | | |
| Perkins..... | 0.803 | 0.806 | 0.815 | 0.843 | 0.875 | 0.889 | 0.876 |
| Cosumne..... | .809 | .811 | .819 | .840 | .875 | .871 | .862 |
| Ukiah..... | .806 | .810 | .824 | .848 | .881 | .891 | .881 |
| Wheatland..... | .809 | .810 | .816 | .845 | .893 | .900 | .895 |
| Oregon..... | .809 | .811 | .816 | .855 | .889 | .895 | .876 |
| New York..... | | .812 | .821 | .853 | .884 | .891 | .876 |
| Imported (Saaz)..... | | | .812 | .832 | .874 | .887 | .878 |

1908 CROP (AT 23° C.).

| | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|
| California: | | | | | | | |
| Perkins..... | 0.802 | 0.805 | 0.809 | 0.834 | 0.883 | 0.871 | 0.866 |
| Cosumne..... | .805 | .804 | .810 | .835 | .884 | .894 | .880 |
| Ukiah..... | .803 | .804 | .808 | .835 | .882 | .888 | .863 |
| Wheatland..... | .805 | .806 | .811 | .837 | .885 | .894 | .882 |
| Oregon..... | .802 | .801 | .806 | .828 | .885 | .890 | .883 |
| New York..... | | .810 | .813 | .842 | .889 | .897 | .897 |
| Washington..... | .803 | .805 | .809 | .835 | .881 | .887 | .874 |
| Imported (Saaz)..... | | .811 | .813 | .840 | .885 | .890 | .876 |

1909 CROP (AT 23° C.).

| | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|
| California: | | | | | | | |
| Perkins..... | 0.812 | 0.815 | 0.821 | 0.844 | 0.879 | 0.863 | 0.876 |
| Cosumne..... | .820 | .822 | .832 | .855 | .891 | .888 | .875 |
| Ukiah..... | .806 | .807 | .810 | .833 | .873 | .891 | .881 |
| Wheatland..... | .803 | .807 | .812 | .831 | .872 | .872 | .888 |
| Oregon..... | .806 | .806 | .811 | .831 | .880 | .894 | .889 |
| New York..... | .823 | .819 | .828 | .859 | .890 | .900 | .886 |
| Washington..... | .808 | .808 | .813 | .836 | .884 | .895 | .883 |
| Imported (Saaz)..... | | .810 | .816 | .837 | .876 | .882 | .872 |

The specific gravity, although less inclined to indicate material differences, at least conveys some idea of the composition of the succeeding fractions. The low-boiling fractions naturally possess the lowest specific gravity, which increases as the constituents of greater density make their appearance in the later fractions. When the specific gravity is fairly constant the fractions may contain similar constituents in similar proportions. A rapid rise during distillation signifies a quick change and a sharp separation of the denser compounds. Sudden increases in specific

gravity from fraction to fraction, as observed in the table, may be construed to mean that a fairly good separation of the denser compounds has taken place. The fractions of the lowest specific gravity in all cases were those boiling below 185° C. This portion of the oil should contain the terpenic constituents if present. Fractions 1, 2, and 3 did not differ greatly from each other through the four seasons, thus indicating a similar composition of the oils. The specific gravity of the oils from the cold-storage samples was greatly different from that of the other oils, being higher in all cases than in the oils from the fresh hops. The specific gravity of fractions 4, 5, and 6 increased very much in the sequence in which they were distilled, comparing very favorably, however, in the different oils. The oxygenated constituents, if present in the oil, would possibly be found largely in fractions 4 and 5, while fractions 6 and 7 should contain sesquiterpene constituents. Fraction 7 showed a decrease in specific gravity, due probably to partial decomposition at the high temperature at which it was distilled.

Curves of the specific gravity were not drawn because of the similarity in the various fractions, the same general course being evident in each oil. In general, the table of results shows that the fractionation of each oil proceeded about the same with regard to the nature of the constituents which distilled over. Although the specific gravities corresponded very closely, it is not necessarily inferred that the oils are alike in composition. The difference may be quantitative rather than qualitative, the size of the fractions determining the quantitative composition of the oils.

OPTICAL ROTATION

The value of the property of optical rotation, though important in most volatile oils, is perhaps lessened when applied to oil of hops, since its constituents are more or less inactive or only slightly active. The rotatory power of each fraction of the oils was carefully determined, and as it was low it was expressed in minutes rather than degrees. The results were tabulated for each season (Table VI) and curves were drawn to facilitate the comparison (figs. 6, 7, 8, and 9).

TABLE VI.—*Specific rotation of fractions of hop oils distilled for the years 1906 to 1909, inclusive.*

1906 CROP.

| Source of hops. | Fraction 1, 165° to 185° C. | Fraction 2, 185° to 205° C. | Fraction 3, 205° to 225° C. | Fraction 4, 225° to 245° C. | Fraction 5, 245° to 265° C. | Fraction 6, 265° to 275° C. | Fraction 7, 275° C. |
|------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------|
| | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. |
| Oregon..... | — 7.6 | —20.7 | —15.9 | + 9.4 | +47.0 | +89.2 | |
| Do. ^a | Inactive | —12.3 | —25.1 | —44.6 | +27.8 | +49.9 | +114.5 |
| New York..... | —11.7 | —15.8 | +42.5 | +60.1 | +34.9 | +52.5 | |
| Imported..... | Inactive | Inactive | +60.0 | +36.6 | +63.0 | +35.9 | |
| Do. ^a | Inactive | — 4.9 | —11.1 | —14.2 | +11.6 | +67.5 | +177.7 |

^a In cold storage 1 year before distillation.

TABLE VI.—*Specific rotation of fractions of hop oils distilled for the years 1906 to 1909, inclusive—Continued.*

| 1907 CROP. | | | | | | | |
|----------------------|----------------------------------|---|---|---|---|---|---|
| Source of hops. | Fraction 1, -165° C. | Fraction 2, 165° to 170° C. | Fraction 3, 170° to 185° C. | Fraction 4, 185° to 225° C. | Fraction 5, 225° to 260° C. | Fraction 6, 260° to 275° C. | Fraction 7, 275° to 290° C. |
| California: | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. | Minutes. |
| Perkins..... | -15.0 | -17.7 | -27.3 | -56.3 | -68.8 | -87.1 | -35.9 |
| Cosumne..... | -12.7 | -23.6 | -35.2 | -43.2 | -54.5 | +33.2 | +38.4 |
| Ukiah..... | -12.8 | -22.7 | -35.2 | -66.0 | -70.8 | -37.3 | +47.1 |
| Wheatland..... | -12.7 | -24.7 | -30.4 | -29.4 | -58.7 | -69.1 | +139.0 |
| Oregon..... | -3.8 | -5.7 | -16.9 | -38.3 | -63.0 | +25.5 | +58.7 |
| New York..... | | | -5.8 | -9.4 | +10.5 | +59.7 | +93.1 |
| Imported (Saaz)..... | | | Inactive | -4.6 | +1.7 | +9.2 | +66.9 |
| 1908 CROP. | | | | | | | |
| California: | | | | | | | |
| Perkins..... | Inactive | Inactive | -20.5 | -44.6 | -66.5 | +28.4 | +28.4 |
| Cosumne..... | -25.5 | -25.6 | -28.8 | -44.5 | -72.6 | -40.0 | +23.4 |
| Ukiah..... | Inactive | -6.2 | -10.6 | -39.5 | -58.7 | +14.7 | |
| Wheatland..... | -25.5 | -30.7 | -38.2 | -64.2 | -84.3 | -25.5 | +28.1 |
| Oregon..... | Inactive | -5.0 | -16.1 | -26.0 | -13.1 | +60.4 | +9.5 |
| New York..... | | -17.7 | -25.5 | -27.0 | +38.7 | +88.5 | +76.9 |
| Washington..... | | Inactive | -18.7 | -27.3 | +37.4 | +79.3 | +71.1 |
| Imported (Saaz)..... | Inactive | -15.2 | -25.3 | -44.7 | +77.9 | +104.7 | +85.1 |
| 1909 CROP. | | | | | | | |
| California: | | | | | | | |
| Perkins..... | Inactive | -9.5 | -24.8 | -51.1 | -66.9 | 4.8 | 23.9 |
| Cosumne..... | -20.5 | -24.8 | -38.9 | -63.0 | -52.5 | 36.4 | 45.7 |
| Ukiah..... | | -13.8 | -20.2 | -39.6 | -75.3 | -41.6 | 21.1 |
| Wheatland..... | -10.2 | -14.3 | -30.5 | -54.8 | -95.2 | -70.0 | 9.6 |
| Oregon..... | Inactive | Inactive | -10.6 | -16.8 | -14.0 | 83.4 | 107.2 |
| New York..... | | -15.1 | -21.9 | -29.3 | -11.4 | 36.6 | 65.4 |
| Washington..... | | -14.8 | -14.8 | -32.5 | 8.3 | 99.6 | 104.1 |
| Imported (Saaz)..... | | | | -17.1 | -37.6 | -13.9 | 47.4 |

Table VI and figures 6, 7, 8, and 9 show that the initial fractions, as a rule, were inactive. This is probably explained by the fact that these fractions consist of terpenes having little or no activity. The rotation of the first fractions was levo, the power to rotate to the left increasing in most cases up to the fifth fraction. This was par-

ticularly true of the California and Oregon oils of the crops of 1907, 1908, and 1909. The New York, Washington, and imported oils had a general tendency to manifest dextro rotation after the fourth fraction, the levo rotation of the former fractions being consistently less than the same fractions of the California and Oregon oils. The dextro rotation of the last three fractions seemed to be higher, in practically all cases, than

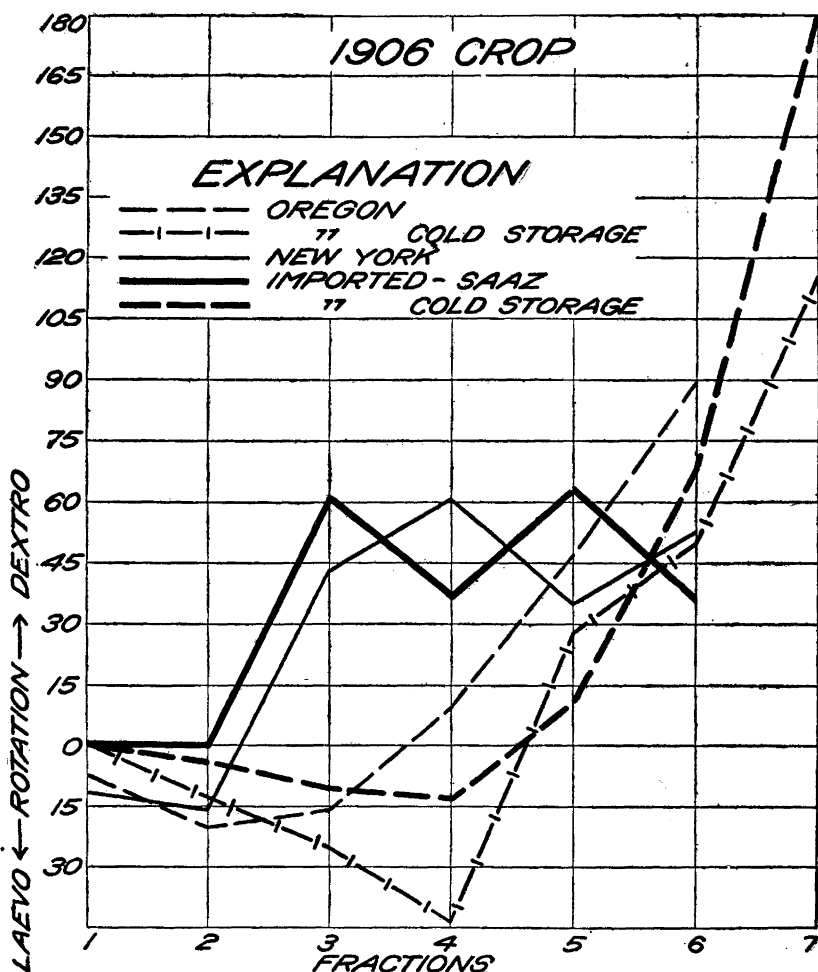


FIG. 6.—Optical-rotation curves of hop oils from the crops of 1906.

the same fractions of California oils. A most noticeable feature was the tendency of the New York oil to follow the same course as the imported oil during each season. The high-boiling portions of the oils, of which the esters and sesquiterpenes form a part, tended to show the greatest rotation. The curves of rotation, as well as the curves of fractionation, show some differences in the various oils, though perhaps in

a lesser degree. This difference appears to be fairly constant from season to season. The same general direction of the California oils during the three seasons is most striking. The curves of the oils of the

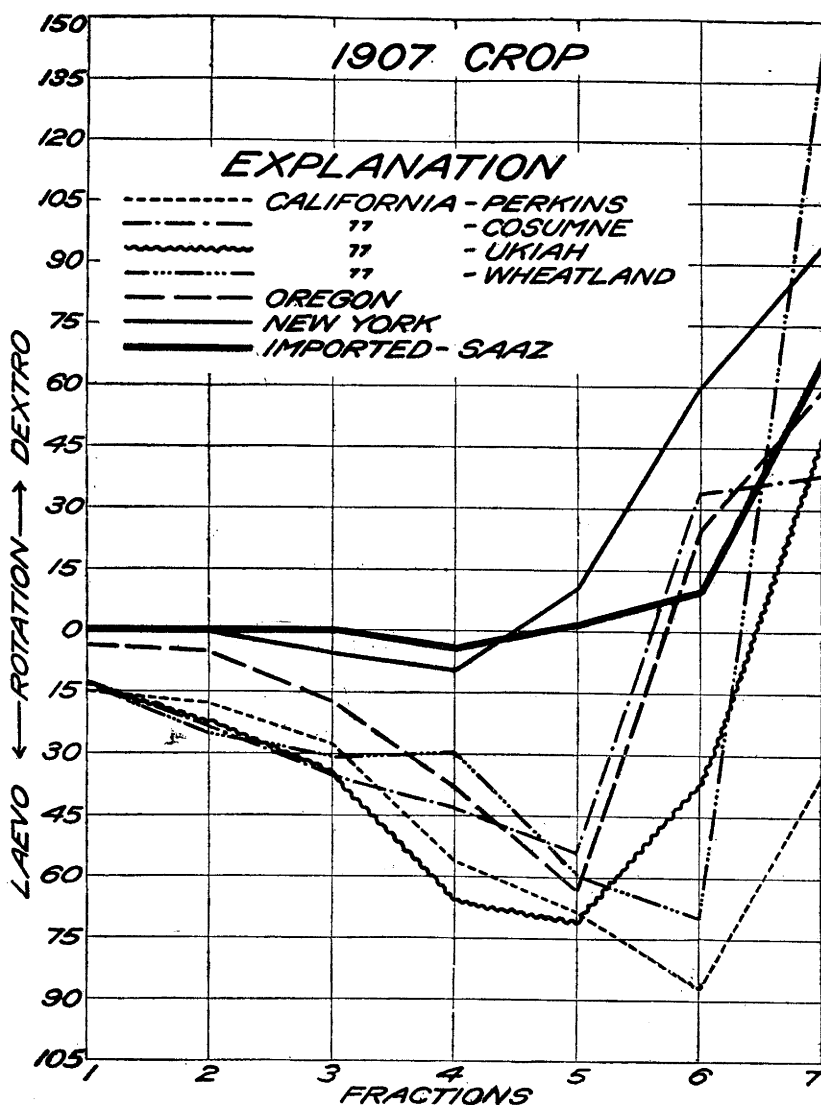


FIG. 7.—Optical-rotation curves of hop oils from the crops of 1907.

1906 crop further emphasize the strong dextro rotation of the oils from the foreign and New York hops as compared with the California and Oregon oils.

CHEMICAL PROPERTIES OF THE FRACTIONS

ACID, ESTER, AND SAPONIFICATION NUMBERS

The chemical properties of the oils and fractions are much more important in determining constant differences or similarities in the volatile oil of hops than the physical properties previously discussed. This is especially true of the aromatic quality of the oil, since quality is dependent upon the ester content. The ester content is expressed in the form

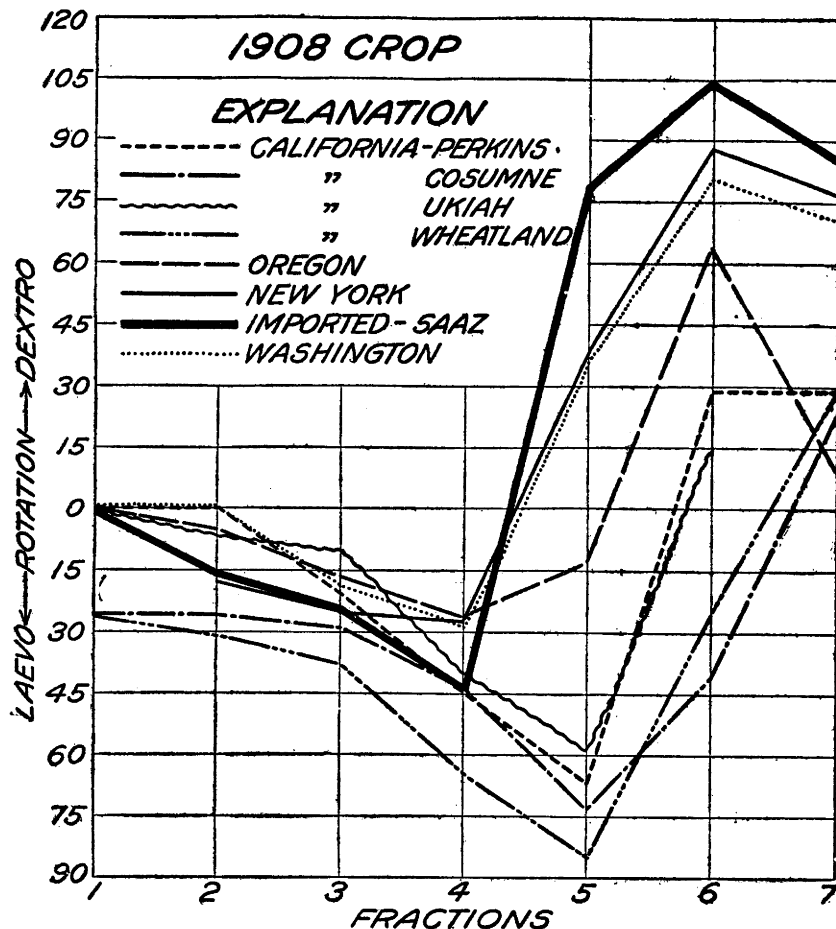


FIG. 8.—Optical-rotation curves of hop oils from the crops of 1908.

of ester numbers based on the amount of esters in 1 gram of the oil. The acid numbers of the fractions are less important, since these depend largely upon the extent of decomposition which the esters undergo during fractionation. Only a small amount of decomposition of the esters is required to liberate sufficient acid to produce high acid numbers, since, as has been shown, the acids in combination with the esters are those of high molecular weight. Owing to the consequent irregularity of the

acid numbers, only little importance can be attached to the results. The saponification numbers, which represent the total saponifiable constituents, including both free acids and esters, should exhibit practically no deviation from the course of the ester numbers. Particular stress is

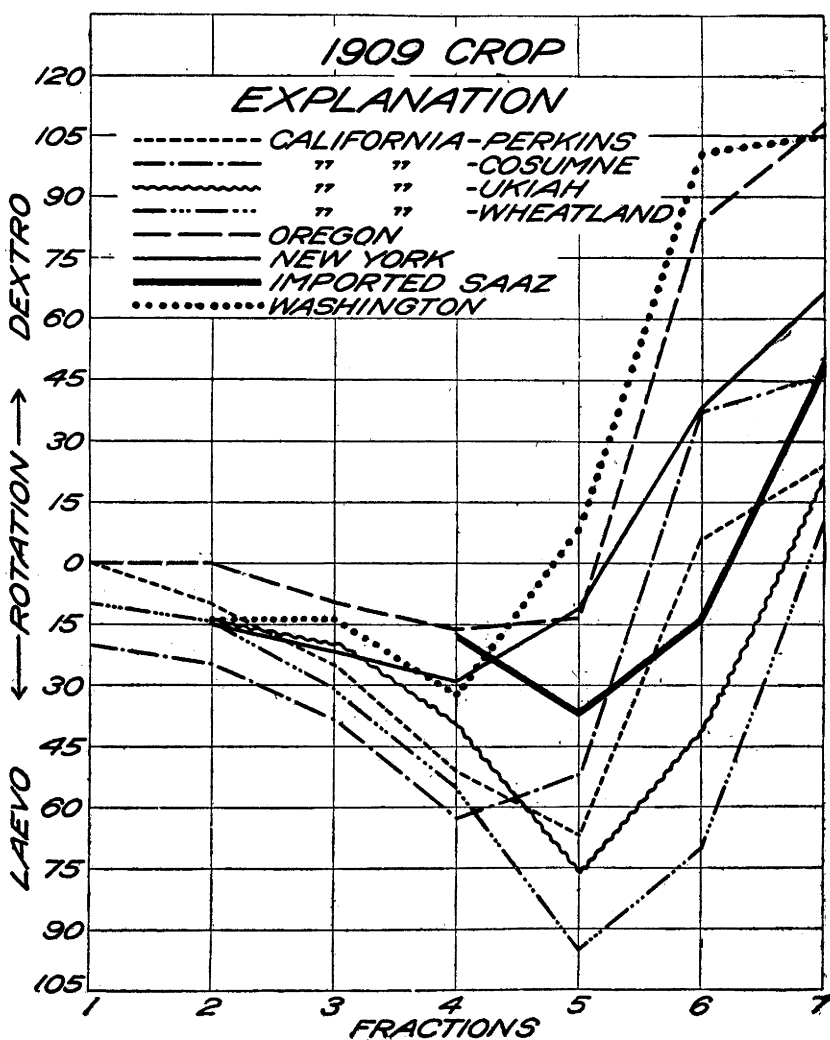


FIG. 9.—Optical-rotation curves of hop oils from the crops of 1909.

therefore placed upon the ester number of the fractions, since these values represent a measurement of the chief odorous constituents of the oils.

The acid, ester, and saponification numbers of the fractions from each individual oil of the seasons of 1906, 1907, 1908, and 1909 are shown in Table VII. Since particular attention is given to the ester numbers, curves were made of this chemical property of the fractions, as shown in figures 10, 11, 12, and 13.

TABLE VII.—*Acid, ester, and saponification numbers of the various fractionated oils from hops for the years 1906 to 1909, inclusive.*

1906 CROP.

| Source of hops. | Fraction 1, 165° to 185° C. | | | Fraction 2, 185° to 205° C. | | | Fraction 3, 205° to 225° C. | | | Fraction 4, 225° to 245° C. | | | Fraction 5, 245° to 260° C. | | | Fraction 6, 260° to 275° C. | | | Fraction 7, 275° to 290° C. | | |
|------------------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|
| | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. |
| | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | |
| Oregon..... | 0.0 | 143.0 | 143.0 | 6.9 | 94.0 | 100.9 | 8.0 | 104.0 | 112.0 | 10.8 | 79.0 | 89.8 | 6.6 | 53.3 | 59.9 | 7.7 | 23.0 | 30.7 | 8.2 | 0.0 | 8.2 |
| Do. ^a | 2.8 | 100.0 | 102.8 | 3.6 | 102.0 | 105.6 | 5.5 | 106.3 | 111.8 | 8.1 | 90.5 | 98.6 | 9.2 | 66.6 | 75.8 | 10.5 | 36.3 | 46.8 | 9.0 | 9.6 | 18.6 |
| New York..... | 0.0 | 84.4 | 84.4 | 3.7 | 70.0 | 73.7 | 14.0 | 79.0 | 93.0 | 8.2 | 41.0 | 49.2 | 7.9 | 23.0 | 30.9 | 5.1 | 14.3 | 19.4 | 7.4 | 0.0 | 7.4 |
| Imported..... | 3.8 | 39.0 | 42.8 | 6.9 | 31.8 | 38.7 | 7.9 | 79.0 | 86.9 | 5.3 | 29.3 | 34.6 | 2.5 | 7.6 | 10.1 | 2.1 | 0.0 | 2.1 | 0.0 | 0.0 | 0.0 |
| Do. ^a | 4.9 | 60.0 | 64.9 | 4.6 | 50.7 | 55.3 | 2.8 | 52.5 | 55.3 | 4.0 | 44.8 | 48.8 | 3.8 | 16.0 | 19.8 | 3.0 | 6.7 | 9.7 | 9.0 | 3.0 | 12.0 |

1907 CROP.

| Source of hops. | Fraction 1, 165° to 185° C. | | | Fraction 2, 185° to 205° C. | | | Fraction 3, 205° to 225° C. | | | Fraction 4, 225° to 245° C. | | | Fraction 5, 245° to 260° C. | | | Fraction 6, 260° to 275° C. | | | Fraction 7, 275° to 290° C. | | |
|----------------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|
| | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. | Acid | | Sap. No. |
| | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | | No. | Ester No. | |
| California: | | | | | | | | | | | | | | | | | | | | | |
| Perkins..... | 0.0 | 42.0 | 42.0 | 0.0 | 48.0 | 48.0 | 0.0 | 53.0 | 53.0 | 1.9 | 94.0 | 95.9 | 1.5 | 68.0 | 69.5 | 3.0 | 40.0 | 43.0 | 1.8 | 11.0 | 12.8 |
| Cosumne..... | 0.0 | 61.0 | 61.0 | 0.0 | 65.0 | 65.0 | 0.0 | 69.0 | 69.0 | 1.7 | 89.0 | 90.7 | 0.0 | 64.0 | 64.0 | 1.8 | 21.0 | 22.8 | 0.0 | 3.5 | 3.5 |
| Ukiah..... | 0.0 | 44.0 | 44.0 | 0.0 | 46.5 | 46.5 | 0.0 | 61.0 | 61.0 | 0.0 | 70.0 | 70.0 | 3.0 | 58.0 | 61.0 | 5.1 | 38.0 | 43.1 | 2.7 | 10.6 | 13.3 |
| Wheatland..... | 2.5 | 53.5 | 56.0 | 1.3 | 54.0 | 55.3 | 1.9 | 58.5 | 60.4 | 2.9 | 69.2 | 72.1 | 4.8 | 48.0 | 52.8 | 6.6 | 18.0 | 24.6 | 7.7 | 5.0 | 12.7 |
| Oregon..... | 2.4 | 62.7 | 65.1 | 1.6 | 65.0 | 66.6 | 1.3 | 68.8 | 70.1 | 1.9 | 91.7 | 103.6 | 2.9 | 75.6 | 78.5 | 4.7 | 27.4 | 32.1 | 4.3 | 10.3 | 14.6 |
| New York..... | | | | 2.1 | 72.9 | 75.0 | 2.6 | 79.6 | 82.2 | 3.7 | 102.4 | 106.1 | 7.0 | 98.0 | 105.0 | 6.9 | 39.1 | 46.0 | 9.8 | 14.1 | 23.9 |
| Imported (Saaz)..... | | | | 2.5 | 23.0 | 25.5 | 3.6 | 23.7 | 27.3 | 1.5 | 33.7 | 35.2 | 1.9 | 30.8 | 32.7 | 2.5 | 13.4 | 15.9 | 3.5 | 7.3 | 10.8 |

^a Hops in cold storage for one year.

TABLE VII.—*Acid, ester, and saponification numbers of the various fractionated oils from hops for the years 1906 to 1909, inclusive—Continued.*

1908 CROP.

| Source of hops. | Fraction 1, -105° C. | | | Fraction 2, 105° to 170° C. | | | Fraction 3, 170° to 185° C. | | | Fraction 4, 185° to 225° C. | | | Fraction 5, 225° to 260° C. | | | Fraction 6, 260° to 275° C. | | | Fraction 7, 275° to 290° C. | | |
|----------------------|-------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|
| | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. |
| California: | | | | | | | | | | | | | | | | | | | | | |
| Perkins..... | 2.4 | 53.4 | 55.8 | 1.7 | 56.8 | 58.5 | 1.0 | 63.7 | 64.7 | 2.8 | 86.6 | 89.4 | 4.7 | 71.6 | 76.3 | 3.6 | 26.0 | 29.6 | 2.4 | 8.0 | 10.4 |
| Costume..... | 2.4 | 40.0 | 42.4 | 2.1 | 46.0 | 48.1 | 1.3 | 50.0 | 51.3 | 3.0 | 60.0 | 63.0 | 4.9 | 60.0 | 64.9 | 4.2 | 51.2 | 55.4 | 4.5 | 3.8 | 8.3 |
| Ukiah..... | 1.0 | 46.0 | 47.0 | .5 | 58.0 | 58.5 | .8 | 58.0 | 58.8 | 1.1 | 78.6 | 79.7 | 2.9 | 71.0 | 73.9 | 2.4 | 23.0 | 25.4 | 2.3 | 3.8 | 6.1 |
| Wheatland..... | 5.5 | 43.0 | 48.5 | 1.4 | 50.0 | 51.4 | 2.0 | 53.5 | 55.5 | 3.2 | 62.5 | 65.5 | 5.2 | 55.7 | 60.9 | 4.1 | 21.4 | 25.5 | 3.8 | 7.3 | 11.1 |
| Oregon..... | .7 | 46.3 | 47.0 | .7 | 48.3 | 49.0 | .9 | 53.2 | 54.1 | 1.1 | 75.4 | 76.5 | 2.4 | 69.4 | 71.8 | 2.1 | 21.3 | 23.4 | 3.4 | 8.0 | 11.4 |
| New York..... | 2.1 | 41.0 | 43.1 | 1.6 | 42.0 | 43.6 | 1.0 | 49.0 | 50.0 | 2.1 | 47.0 | 49.1 | 4.0 | 64.0 | 68.0 | 3.5 | 24.0 | 27.5 | 4.0 | 10.0 | 14.0 |
| Washington..... | 1.9 | 50.3 | 52.2 | 1.7 | 56.0 | 57.7 | 1.0 | 67.5 | 68.5 | 1.6 | 92.0 | 93.6 | 2.8 | 82.0 | 84.8 | 2.5 | 27.8 | 30.3 | 3.7 | 7.0 | 10.7 |
| Imported (Saaz)..... | 3.6 | 34.0 | 37.6 | 1.7 | 41.4 | 43.1 | 1.1 | 45.7 | 46.8 | 1.6 | 58.6 | 60.2 | 4.0 | 60.8 | 64.8 | 4.0 | 28.0 | 32.0 | 2.3 | 5.4 | 7.7 |

1909 CROP.

| Source of hops. | Fraction 1, -105° C. | | | Fraction 2, 105° to 170° C. | | | Fraction 3, 170° to 185° C. | | | Fraction 4, 185° to 225° C. | | | Fraction 5, 225° to 260° C. | | | Fraction 6, 260° to 275° C. | | | Fraction 7, 275° to 290° C. | | |
|----------------------|-------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|--------------------------------|--------------|-------------|
| | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. | Acid No. | Ester No. | Sap. No. |
| California: | | | | | | | | | | | | | | | | | | | | | |
| Perkins..... | 7.4 | 77.0 | 84.4 | 3.0 | 80.0 | 83.0 | 1.6 | 96.0 | 97.6 | 2.0 | 101.0 | 103.0 | 3.2 | 103.0 | 106.2 | 2.3 | 24.0 | 26.3 | 1.6 | 2.8 | 4.4 |
| Costume..... | 11.7 | 82.0 | 93.7 | 8.0 | 96.0 | 104.0 | 5.0 | 104.7 | 109.7 | 4.6 | 120.0 | 124.6 | 5.9 | 87.0 | 92.9 | 6.9 | 28.0 | 34.9 | 4.0 | 3.0 | 7.0 |
| Ukiah..... | 2.4 | 54.7 | 57.1 | 2.7 | 58.0 | 60.7 | 1.5 | 62.4 | 63.9 | 2.2 | 76.5 | 78.7 | 3.5 | 73.0 | 76.5 | 3.2 | 36.0 | 39.2 | 3.5 | 10.0 | 13.5 |
| Wheatland..... | 2.8 | 59.0 | 61.8 | 1.7 | 59.0 | 60.8 | .9 | 64.8 | 65.7 | 1.8 | 80.3 | 82.1 | 2.4 | 84.0 | 86.4 | 3.3 | 55.3 | 58.6 | 2.3 | 9.3 | 11.6 |
| Oregon..... | 2.1 | 53.0 | 55.1 | 1.5 | 60.0 | 61.5 | 1.2 | 66.0 | 67.2 | 1.8 | 67.0 | 68.8 | 3.4 | 77.6 | 81.0 | 3.5 | 33.3 | 36.8 | 5.4 | 11.0 | 16.4 |
| New York..... | 10.1 | 66.3 | 76.4 | 8.4 | 71.6 | 80.0 | 6.3 | 85.8 | 92.1 | 5.4 | 100.0 | 105.4 | 6.4 | 78.4 | 84.8 | 8.0 | 30.2 | 38.2 | 9.4 | 9.0 | 18.4 |
| Washington..... | 1.7 | 50.8 | 52.5 | .5 | 55.5 | 56.0 | .5 | 61.7 | 62.2 | 1.5 | 80.4 | 81.9 | 3.0 | 75.2 | 78.2 | 3.0 | 33.0 | 36.0 | 4.8 | 9.9 | 14.7 |
| Imported (Saaz)..... | | | | 3.9 | 32.3 | 36.2 | 3.0 | 41.9 | 44.9 | 3.7 | 56.0 | 59.7 | 4.1 | 47.5 | 48.6 | 3.8 | 20.0 | 23.8 | 4.0 | 7.5 | 11.5 |

COMPARISON OF THE ACID, ESTER, AND SAPONIFICATION NUMBERS OF THE FRACTIONS

The acid numbers of the fractions during each year are most variable; hence difficulty is encountered in attempting a comparison of the oils by this means. From the table it is quite obvious that the oils which in their original conditions possessed free acidity (as indicated by the high acid numbers) show much more decomposition of esters with the liberation

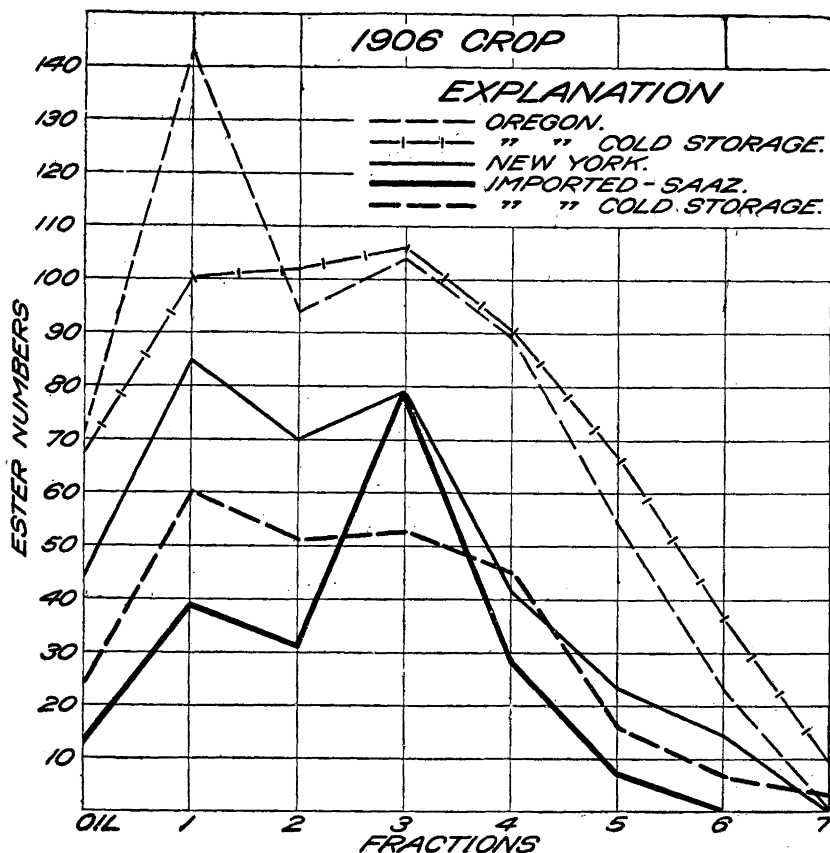


FIG. 10.—Ester-number curves of hop oils from the crops of 1906.

of free acids than do the oils with less acidity or with none. The acid numbers of the fractions of these high-acid oils are in all cases notably higher than those of similar fractions of the other oils. It is therefore very probable that oils with high acid numbers are much less stable than those free from acidity. This may in turn be true of the hops from which the oils were distilled. No particular oil appears to show a regular increase or decrease in acidity of the fractions, hence it is most difficult to draw conclusions from these values.

In direct contrast with the irregularity of the acid numbers of the various fractions there is a remarkable regularity of the ester numbers from year to year. There is also a most notable regularity of increase

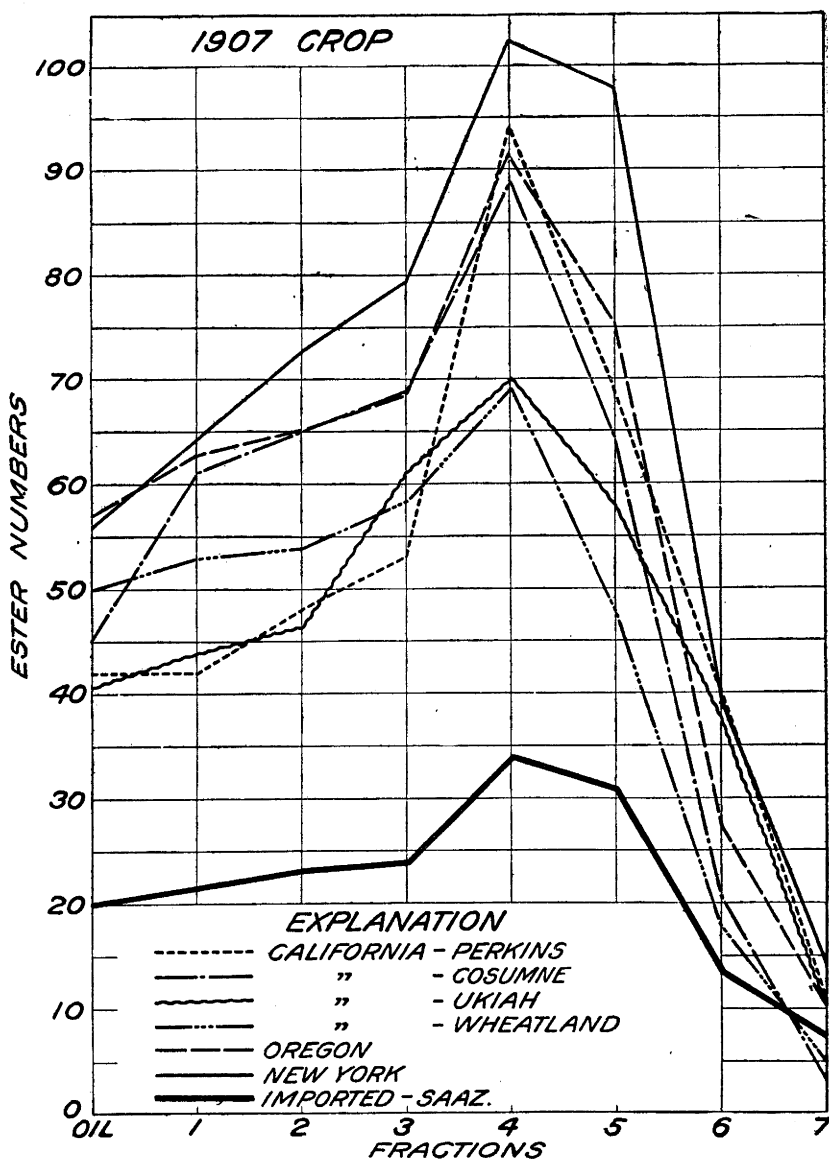


FIG. 11.—Ester-number curves of hop oils from the crops of 1907.

in ester numbers as the particular fractions are approached in which the boiling point most nearly corresponds to those of the esters present. A correspondingly regular decrease is noted in each succeeding fraction from this point to the highest boiling fraction. This is clearly shown by

the curves in figures 10, 11, 12, and 13. These curves show the ester numbers of the original oils and the fractions obtained from each oil, the general direction being the same in each season. Figures 11, 12, and 13 show the great similarity from year to year of the ester numbers and fractions of the oils from the same section. (See also fig. 1.) It will be

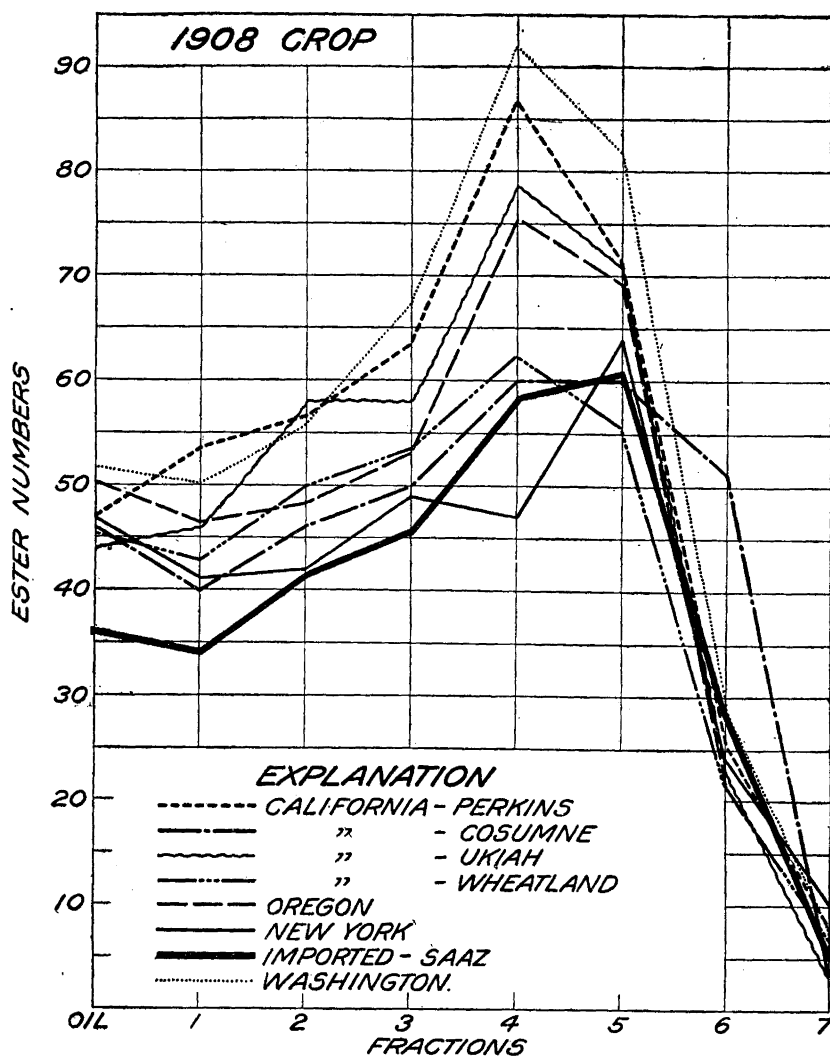


FIG. 12.—Ester-number curves of hop oils from the crops of 1908.

observed that a very close relationship exists between the oils and the fractions from any particular locality. The amount of esters increases as the fractionation proceeds until fraction 4 is reached, after which the quantity decreases until there is practically none in fraction 7. Apparently the oil highest in esters distills between the temperatures of 185° and

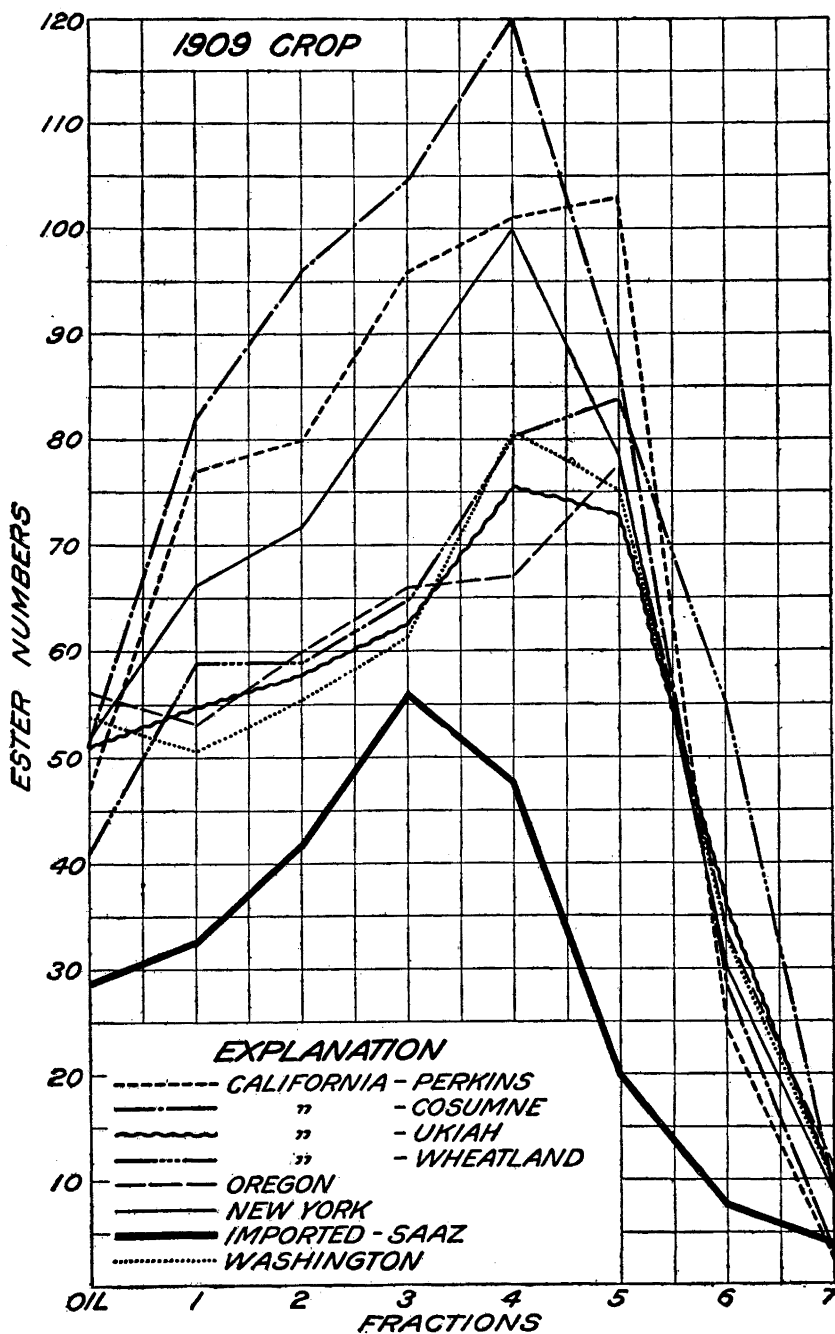


FIG. 13.—Ester-number curves of hop oils from the crops of 1909.

225° C., a considerable amount of esters, however, appearing also in the preceding fractions.

That the fractionation proceeded with fair regularity in each oil is shown by the relationship between the ester numbers of each fraction and the general direction of the curves, which is the same in all the oils.

During the three seasons the curves seem to group themselves according to the source of the hops, those of the oils which differ most in ester content being separate from the others. The course of the curves is therefore, in a sense, an indication of the source of the hops. Throughout the several seasons the curve of the imported hops is conspicuous by its low position as compared with the curves of the oils from the American hops. While it can not be stated with certainty that the oil from the imported hops would continue to show this low ester content, it is very probable that the same differences would continue, since nine samples from five successive seasons all yielded oils poorer in esters than the oils from the American hops during the same seasons.

CHEMICAL EXAMINATION OF THE OIL

FREE ACIDS

A small amount of free acids is contained in the oil of hops. In order to identify, if possible, these free acids, the oil was shaken out with an aqueous solution of sodium carbonate. The alkaline liquid was subsequently acidified and distilled with steam. The aqueous distillate, which was acid to litmus paper, was neutralized with sodium hydroxid and precipitated with silver-nitrate solution. By ignition of the dried silver salts, traces of formic and heptonic acids were observed, but the bulk of the volatile acids was identified as valerianic acid, 52 per cent of silver salt being obtained. (Silver valerianate requires 51.6 per cent of silver.) Formic acid was further identified by the formation of a silver mirror from ammoniacal silver-nitrate solution and by the reduction of mercuric chlorid to mercurous chlorid.

COMBINED ACIDS

After saponifying a quantity of the oil with alcoholic potassium hydroxid, diluting with water, and separating the unsaponified portion of the oil, the resulting alkaline liquid was evaporated to a small volume. Acidification with sulphuric acid caused the separation of an oily layer on the surface of the liquid. The oily acids thus separated had a pronounced odor of some of the higher fatty acids. After separation of the oily layer from the aqueous distillate by means of a separatory funnel, the distillate was shaken out with ether to remove traces of the insoluble fatty acids. The liberation of such a large quantity of oily acids shows that the esters of the oil are for the most part in combination with acids of a higher molecular weight which are oily in character and are sparingly soluble in water.

After neutralization and fractional precipitation with silver-nitrate solution, the aqueous distillate representing the soluble volatile combined acids produced small amounts of silver salts which contained 66 and 71 per cent of silver, respectively. The combined soluble acids therefore consisted largely of formic acid with a trace of acetic acid.

The oily acids previously mentioned, which represented the bulk of the combined acids, corresponded to 5 per cent of the total oil saponified. A small amount of the oily acids, which had a most unpleasant, repulsive odor, was neutralized with potassium-hydroxid solution. The neutralized solution was then precipitated fractionally with silver-nitrate solution. The first two fractions precipitated, which were the smallest and represented the most insoluble salts, yielded 38.5 and 39.2 per cent of silver, corresponding to decylic (caprinic) acid. (Silver salt of decylic acid contains 38.6 per cent of silver.) The third and fourth fractions of silver salts assayed 40.3 and 40.9 per cent of silver. These results correspond very closely to nonoic (pelargonic) acid, whose silver salt contains theoretically 40.7 per cent of silver. Fractions 5 and 6, containing 41.6 and 44 per cent of silver, respectively, had perhaps traces of the preceding nonoic and succeeding lower acids. In all probability a portion of these fractions consisted of octoic (caprylic) acid, which theoretically requires 42.9 per cent of silver. The final fractions both gave 46 per cent of silver, which corresponds well with heptoic (œnanthylic) acid. This acid contains theoretically 45.5 per cent of silver. Based on the total weight of all precipitates, it appears that the oily acids in combination as the esters in the oil of hops consist of about equal proportions of heptoic, octoic, and nonoic acids, with a somewhat smaller content of decylic acid.

Analyzing the fractions of a fractionated oil in another experiment for both free and combined acids, these results were verified in every respect, and additional acids were identified. In the lower boiling fractions butyric acid was identified among the free acids in addition to the formic, valerianic, and heptoic acids previously mentioned.

Heptoic, octoic, and nonoic acids were formed in the free state in the higher boiling fractions, due probably to the splitting off of these acids from the esters at the high heat of distillation. The insoluble acids in all the fractions consisted largely of heptoic and nonoic acids, with some octoic acid, the highest boiling fractions containing two higher acids, decylic and undecylic.

FRACTIONATION OF SAPONIFIED OIL

The saponified oil remaining after separation of the acids was twice fractionated with a 3-bulb Ladenburg flask, and the results are given in Table VIII.

TABLE VIII.—*Fractionation of saponified oil of hops, showing physical properties of the fractions.*

| Frac- tion. | Tempera- ture. ^a | Dis- tilled over. | Specific gravity at 22° C. | Rotat- ion in 50-mm. tube. | Refrac- tion ND 22° C. | Remarks. |
|----------------|--------------------------------|-------------------------|----------------------------------|-------------------------------------|---------------------------------|--|
| | °C. | Per cent. | | Min- utes. | | |
| 1..... | Below 160 | 4.0 | 0.8096 | —21.7 | 1.4615 | A large portion of this fraction distilled below 100° C. Strong irritating odor. |
| 2..... | 160 to 165 | 15.5 | .8180 | —21.7 | 1.4710 | } Mild aromatic, pleasant yet peculiar odor, unlike any of the common terpenes. |
| 3..... | 165 to 170 | 15.0 | .8093 | —23.9 | 1.4703 | |
| 4..... | 170 to 175 | 2.7 | .8440 | —28.0 | 1.4750 | Pleasant odor, similar to preceding fraction. |
| 5..... | 175 to 185 | 2.2 | .8504 | —33.2 | 1.4752 | More strongly aromatic, pleasant. |
| 6..... | 185 to 195 | 2.1 | .8767 | | 1.4799 | Distilled largely at 195° C. Pleasant hoplike odor. |
| 7..... | 195 to 205 | .9 | .9060 | —45.6 | 1.4836 | Distilled uniformly. Pleasant odor, reminding of hops. |
| 8..... | 205 to 215 | .7 | | | 1.4865 | Distilled mostly from 205° to 210° C. Odor pleasantly aromatic, less fragrant. |
| 9..... | 215 to 245 | 2.2 | .8680 | —45.6 | 1.4818 | Temperature rose rapidly to 245° C. Odor less pleasant. |
| 10.... | 245 to 255 | 2.7 | .8860 | —23.9 | 1.4878 | Distilled uniformly. Odor strong and rather disagreeable. |
| 11.... | 255 to 265 | 5.3 | .8740 | —2.1 | 1.4871 | Distilled uniformly. Odor strong and unpleasant. |
| 12.... | 265 to 275 | 6.0 | .8850 | +10.3 | 1.4947 | Distilled largely between 265° and 270° C. Not strongly aromatic, disagreeable. |
| 13.... | 275 to 285 | 3.2 | .8870 | +6.9 | 1.4948 | Disagreeable odor. |
| 14.... | 285 to 295 | 3.8 | .8930 | +7.6 | 1.4973 | Heavy oil with rather strong, unpleasant odor. |
| 15.... | 295 to 305 | 2.8 | .8940 | +8.2 | 1.5000 | Heavy oil with repulsive odor. |

^a Residue 305° and over.

ALDEHYDE CONSTITUENTS

The initial distillate, which had a most irritating and penetrating action upon the nasal passages, was tested for reducing properties. A silver mirror was readily produced with silver nitrate, and a decolorized solution of fuchsin (magenta solution) became bright red immediately. Lebbin's solution (5 per cent resorcin in a solution of 40 to 50 per cent of sodium hydroxid) produced a deep-red color, characteristic of formaldehyde.

IDENTITY OF TERPENE HYDROCARBON WITH MYRCENE

The boiling points of the second and third fractions signified a terpenic character, but the odor was unlike that of the usual terpenes. An elementary analysis gave the following results:

Fraction 2.—Carbon, 87.5 per cent; hydrogen, 10.7 per cent.

Fraction 3.—Carbon, 86.4 per cent; hydrogen, 11.9 per cent.

While it must be remembered that these fractions were not pure, the percentage of carbon and hydrogen nevertheless points to terpene composition, since $C_{10}H_{16}$ requires 88.1 per cent of carbon and 11.7 per cent of hydrogen.

Preparation of the nitrosochlorid and other crystalline terpene derivatives with bromin and halogen acids failed in all cases. This, together with the unusually low specific gravity, pointed to another class of related hydrocarbons belonging to the aliphatic series. Aliphatic hydrocarbons with the same empirical formula, $C_{10}H_{16}$, are termed the "olefinic terpenes." The presence of olefinic terpenes in volatile oils was first observed by Power and Kleber (1895), who isolated a hydrocarbon from oil of bay, which was termed "myrcen." Chapman (1903) mentioned this hydrocarbon as a constituent of oil of hops.

In order to compare the hydrocarbon myrcene of bay oil with the hydrocarbon from hop oil, the properties of the respective compounds were tabulated as given in Table IX.

TABLE IX.—*Comparison of the properties of hydrocarbon from oil of hops with the olefinic hydrocarbon myrcene.*

| Properties. | Hydrocarbon from oil of hops. | Myrcene. |
|---------------------------------|---|---|
| Boiling point..... | 165° to 170° C..... | 171° C. |
| Specific gravity..... | 0.8093 at 22° C..... | 0.8023 at 15° C. |
| Index of refraction..... | 1.4703..... | 1.4673. |
| Rotation (50-mm. tube)... | −23.9'..... | Inactive. |
| Color and behavior on standing. | Colorless, becoming slightly yellow and changing to a viscous mass. | Colorless, becoming yellow and resinifying. |

A very close relationship is observed between the boiling point and the specific gravity of the two compounds. The slight discrepancies which exist, especially in the rotation, are probably due to some impurity of the fraction. The most striking characteristic of the hydrocarbon is its instability. The tendency to polymerize was most marked, the respective fractions in the large number of oils fractionated becoming viscous and almost solid in a comparatively short time. This peculiar property was observed by Power and Kleber (1895) in their experiments with the hydrocarbon from bay oil. It was also exhibited in oil of hops, which became viscous, even when the usual precautions were taken against light and air.

Since the properties of the hydrocarbon from the oil of hops show such a close resemblance to those of myrcene, it can be stated with comparative certainty that the terpene hydrocarbon, which represents the large proportion of the lower-boiling constituents, is identical with the olefinic terpene myrcene. By reference to the curves of fractionation of the various oils (figs. 2, 3, 4, and 5) it will be observed that in practically all cases myrcene constitutes the largest portion of the oils.

IDENTITY OF ALCOHOL AND ESTERS OF HOP OIL WITH MYRCENOL AND ITS ESTERS

If present in the oil, oxygenated constituents should have a tendency to concentrate themselves in the fractions above the temperature of 185°C . Therefore fractions 6, 7, and 8 were analyzed in order to determine their elementary composition. Granting that the separation of constituents is at most only partially effected by fractionation, the determination of the carbon and hydrogen content of these fractions should show the presence or absence of oxygenated compounds. The oxygenated compounds of a saponified oil are usually alcohols of the formula $\text{C}_{10}\text{H}_{18}\text{O}$. The fractions in question gave the following results:

Fraction 6.—Carbon, 81.7 per cent; hydrogen, 11.1 per cent.

Fraction 7.—Carbon, 80.0 per cent; hydrogen, 10.6 per cent.

Fraction 8.—Carbon, 81.4 per cent; hydrogen, 11.3 per cent.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires 77.8 per cent of carbon and 11.7 per cent of hydrogen. The somewhat higher carbon content of the fractions may be explained by the fact that adhering traces of hydrocarbons were not completely separated in the earlier fractions. Oxygenated constituents of the nature of alcohols with the composition $\text{C}_{10}\text{H}_{18}\text{O}$ are strongly indicated in the fractions mentioned.

Since Barbier (1901) states that myrcene is capable of being hydrated chemically with the formation of an alcohol $\text{C}_{10}\text{H}_{18}\text{O}$, called "myrcenol," it was thought that the alcohol of hop oil might be allied to this compound. Furthermore, it is possible that an alcohol like myrcenol could occur in company with the terpene myrcene, from which it is capable of being prepared.

For a further comparison of the above fractions with myrcenol, Table X was prepared.

When it is remembered that the fractions contain admixtures of other constituents incapable of being separated by fractionation, the properties of the fractions compare very favorably with those of myrcenol. Sufficient similarity exists among the various properties, especially the boiling point, specific gravity, and refraction, to indicate the presence of an alcohol similar to myrcenol in the fractions recorded.

In this connection it was deemed advisable to call attention to the esters of the oil of hops, which are present in considerable proportion, and to compare the chief ester fractions of the oil with the acetic ester of myrcenol. As the fractionation of the oil proceeded, it was observed that the esters concentrated themselves in the fractions boiling at 185° to 225° and 225° to 260°C . Although the fractions were by no means pure esters, a comparison of the physical properties with those of the known esters of myrcenol shows that the esters of the oil boil at much higher temperatures than free alcohol. This is readily explained when

cognizance is taken of the fatty acids identified, whose boiling points are exceedingly high. Thus the boiling point of heptioic acid is 221° , of octoic acid 237° , and of nonoic acid 253° C. A combination of these acids with myrcenol, which boils at 213° to 215° C., would tend to produce esters with a boiling point much higher than the alcohol itself. The comparison of the chief ester fractions of hop oil with the acetic-acid ester of myrcenol is given in Table XI.

TABLE X.—*Comparison of the physical and chemical properties of alcohol fractions from hop oil with the alcohol myrcenol.*

| Boiling points of hop oil fractions and myrcenol. | Specific gravity at 22° C. | Rotation in 50-mm. tube. | Refraction at 22° C. | Description. |
|---|-------------------------------------|--------------------------|-------------------------------|---|
| Alcohol fractions from hop oil: | | | | |
| 185° to 195° C. | o. 8767 b. 9060 | a-45.6 | 1. 4799 | Nearly colorless; oily liquid with pleasant hoplike odor, becoming viscous on standing. |
| 195° to 205° C. | | | 1. 4836 | Slightly yellowish liquid with characteristic hop aroma, becoming viscous on standing. |
| 205° to 215° C. | | | 1. 4865 | Heavy yellowish oil with agreeable odor of hops, becoming very viscous on standing. |
| Myrcenol, 213° to 215° C. (99° to 101° C. at 10 mm.). | c. 9012 | | c 1. 4778 | Colorless oily liquid, very odorous; polymerizes, slowly becoming viscous. |

a Rotation of combined fractions, 185° to 215° C.

b Specific gravity of combined fractions, 195° to 215° C.

c At 14.5° C.

TABLE XI.—*Comparison of the chief ester fractions of hop oil with the acetic-acid ester of myrcenol.*

| Fractions and ester of myrcenol. | Boiling point. | Description. |
|-------------------------------------|-------------------------------------|--|
| Chief ester fractions from hop oil: | | |
| Fraction 4. | 185° to 225° C... | Slightly yellow oily liquid with agreeable hoplike odor. |
| Fraction 5. | 225° to 260° C... | Pale brownish liquid with strong hop odor. |
| Myrcenyl acetate. | a 231° C. | Colorless oily liquid with strong odor. |

a 112° C. at 10 mm.

It is very probable that esters of the higher acids, as heptoic, octoic, and nonoic, would boil at higher temperatures than myrcenyl acetate. This would necessitate the concentration of the esters in fractions, as shown above. Earlier fractions would also contain some esters, as would later fractions, since the association of lower and higher boiling compounds with the esters would modify their boiling points. In order to show that the esters constitute no small proportion of the oil, curves of fractionation were made of the original oil (containing esters) and the same oil after saponification of the esters (fig. 14).

The curves show directly opposite courses from each other between the temperatures 170° and 260° C. It was between these temperatures that the large proportion of the esters of the original oil distilled over.

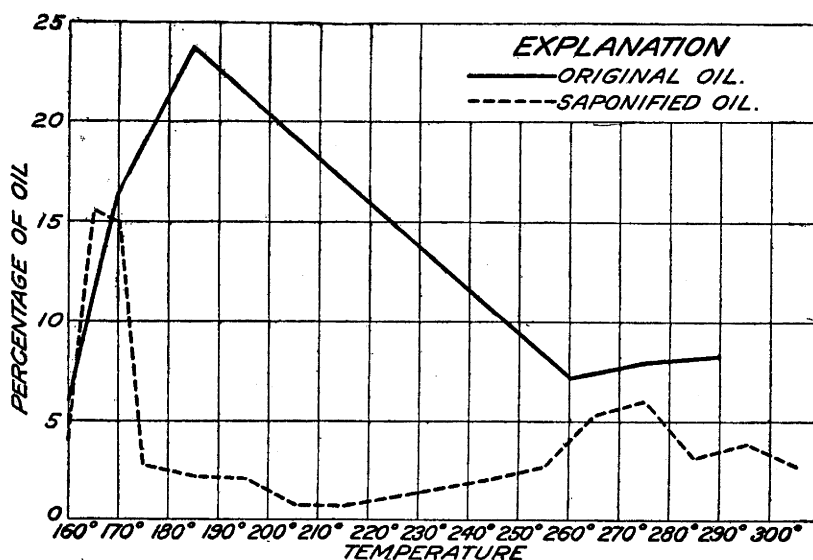


FIG. 14.—Fractionation curves of original and saponified hop oils.

It can therefore be readily perceived that a destruction of these esters by saponification and the consequent removal of the high-boiling acid portion of the esters would tend to flatten the curve of fractionation between these respective points.

The presence of the esters of myrcenol in the oil of hops is not surprising when it is known that the hydrocarbon myrcene, found in the low-boiling fractions, can be readily changed to myrcenol by the action of glacial acetic acid and dilute sulphuric acid. Myrcene bears the same relation to the alcohol myrcenol that camphor does to isoborneol and pinene or that dipentene bears to terpineol. It is very likely that the hydrocarbon myrcene is partly changed to myrcenol by hydration during the formation of the essential oil in the plant, the myrcenol in turn being esterified by the organic acids present.

The reason that it was impossible to quantitatively acetylate the oil was either because there was no free myrcenol present in the oil or because this alcohol would not acetylate without partial decomposition. The latter is probably the case, since in the experiments it was observed that the fractions containing the alcohol and esters were very unstable and readily polymerized to a viscous liquid. Furthermore, these fractions invariably gave negative results when acetylation was attempted.

IDENTIFICATION OF HUMULENE

Combustion of fractions 9 to 16 gave from 84 to 87.6 per cent of carbon and 11.2 to 11.8 per cent of hydrogen. The theoretical requirement of a sesquiterpene $C_{15}H_{24}$ is 88.1 per cent of carbon and 11.8 per cent of hydrogen. It is probable, therefore, that the fractions consisted of a sesquiterpene with inseparable quantity of alcohols, probably sesquiterpene alcohols which would have a tendency to lower the percentage of carbon. The hydrogen content would remain practically the same for the four classes of compounds—the terpenes, alcohols, sesquiterpenes, and sesquiterpene alcohols. Since the sesquiterpene humulene has been mentioned as a constituent of hop oil, a comparison was made between the physical properties of the high-boiling fractions of the saponified oil and the humulene obtained from different sources, the results being given in Table XII.

TABLE XII.—*Comparison of the physical properties of high-boiling fractions of hop oil with those of humulene.*

| Properties. | Fractions of saponified hop oil. | | | | | Humulene. | |
|---|----------------------------------|-----------------|-----------------|-----------------|-----------------|---|--|
| Boiling points of fractions and humulene. | 255° to 265° C. | 265° to 275° C. | 275° to 285° C. | 285° to 295° C. | 295° to 305° C. | From hop oil. ^a 261° to 265° C. | From oil of poplar buds. ^b 263° to 269° C. |
| Specific gravity at 22° C. | 0.8740 | 0.8850 | 0.8870 | 0.8930 | 0.8940 | 0.8987 | 0.8926 |
| Rotation ^d | -2.1 | +10.3 | +6.9 | +7.6 | +8.2' | +1° 2' | +10° 48' |
| Refraction at 22° C. . | 1.4871 | 1.4947 | 1.4948 | 1.4973 | 1.5000 | 1.4978 | |

^a Chapman (1893).

^b Fichter and Katz (1899).

^c At 15° C.

^d Rotation of hop oil fractions determined in 50 mm. tubes.

^e 200-mm. tube.

Close relationship exists between the physical properties of the fractions of hop oil and those of humulene obtained from both oil of hops and oil of poplar buds. It is possible that traces of sesquiterpene alcohols occur in the fractions of the highest boiling points, since the boiling

points of certain sesquiterpene alcohols correspond very closely to these. Thus, cedrol, the sesquiterpene alcohol obtained from cedar-wood oil, boils at 282° , and santalol, obtained from oil of santal wood, boils at 301° C. The possible presence of sesquiterpene alcohols is also indicated by the low carbon content of these fractions, as shown by the elementary analysis. In order to positively identify the sesquiterpene humulene in oil of hops, three high-boiling fractions (225° to 245° , 245° to 260° , and 260° to 275° C.) of several unsaponified oils were used. Petroleum ether solutions of these fractions were treated with a concentrated solution of sodium nitrite with an equal volume of glacial acetic acid added in small portions and vigorously agitated, the mixture being kept well cooled. In fraction 245° to 260° there appeared blue needle-shaped crystals, which melted at 125° C. This is in accordance with the melting points of humulene nitrosite recorded by Chapman (1895b, p. 783) and by Fichter and Katz (1899), which are, respectively, 120° and 127° C. The characteristic blue coloration of the fraction from which the crystals were obtained was produced in each case.

APPROXIMATE COMPOSITION OF THE OIL

From the foregoing analysis of the oil of hops it appears that it has approximately the following composition:

FREE ACIDS.—Chiefly valerianic, with traces of formic, butyric, and heptonic acids.

COMBINED ACIDS (in form of esters).—Chiefly heptonic (œnanthylic) and nonoic (pelargonic) and somewhat smaller quantities of octoic (caprylic), some decylic (caprinic) and undecylic acids, with traces of formic and acetic acids.

ALDEHYDES.—Formaldehyde in the lowest boiling fraction.

HYDROCARBONS.—Myrcene (olefinic terpene), 30 to 50 per cent. Humulene (sesquiterpene), 15 to 25 per cent.

ESTERS.—Chiefly heptonic, octoic, and nonoic acid esters of the alcohol myrcenol, to the extent of 20 to 40 per cent. From the ester number (44) of the oil in question the amount of esters calculated as the heptonic-acid ester of myrcenol was found to be 21 per cent. If calculated as the octoic or nonoic acid esters, the percentage would be considerably augmented.

ALCOHOLS.—Probably myrcenol and a small proportion of sesquiterpene alcohols.

RELATION OF THE VOLATILE OIL TO THE SOURCE OF THE HOPS

From the data presented it is clearly evident that the geographical source of hops has a pronounced effect upon the volatile oil and hence also upon the odor of the hops. The oils distilled from hops of different origin have been shown to possess like constituents, which, however, exist in sufficiently varying proportions to impart a decided difference to the properties of the oil. These differences appear to be constant from season to season, not only in the physical properties but also in the more important chemical properties. Most conspicuous among the chemical properties is the ester value, which is closely related to the odor. The ester content is the most influential factor in modifying the odor of the oils and

consequently that of the hops. It is usually acknowledged that hops of foreign origin possess a more agreeable odor than American hops. The difference in odor always seems to be perceptible although the odor is closely related to that of American hops. That the difference in odor is due to a difference in the volatile oil present can scarcely be questioned; in fact, it has been shown that such is the case. This is not, however, the only instance among aromatic plants where geographical source, with the different conditions of climate and soil, shows its effect in the differences in volatile oils distilled from the plants, as, for example, lavender and peppermint. Not only do hops of foreign origin produce oils noticeably dissimilar in some of their properties from the American oils, but hops grown even in separated sections of the United States have a different odor and yield oils with more or less constant differences from year to year.

CONCLUSIONS

The volatile oil of hops has been shown to consist chiefly of the terpene myrcene, the heptolic, octolic, and nonolic acid esters of the alcohol myrcenol, and the sesquiterpene humulene, with traces of free acids, formaldehyde, and probably some free alcohols. The constituents of chief importance as regards odor are the above-named esters, which constitute a large portion of the oil.

The several oils examined have been found to contain varying proportions of the esters as well as the terpene myrcene and the sesquiterpene humulene. Although no great importance can be attached to the two latter constituents, the variable content of esters is most significant, since the quality of the odor is probably most greatly influenced by them.

Important differences in the oils are apparent not only during any particular season but for several seasons. These constant differences are shown most forcibly in the curves of the physical and chemical properties of the oils. The curves of fractional distillation, which may be said to represent a partial quantitative separation of the chief constituents, bring out strongly the relationship which exists between the hops from any source during one season or several seasons. The optical rotation curves also show this relationship. In general the physical properties of the oils—the fractionation, specific gravity, and optical rotation—show strong similarities which may exist among related oils or strong dissimilarities among unrelated oils. The esters being regarded as the constituents of most importance in affecting the odor of the hops from which the oils were distilled are compared by means of the ester numbers. The curves of the ester content of the various oils and fractions of the oils show at a glance the remarkable differences in the oils from the several geographical sources. The courses followed by the imported oils are most conspicuous because of their constantly lower ester content. More remarkable is the fact that the ester content of the imported oils

remains lower from year to year, practically every sample under observation possessing an exceedingly low ester value. The oils from the California hops are both physically and chemically very similar from season to season. Those from the various sections of California show no important differences in their properties during any particular season, the curves showing considerable parallelism. The Oregon and Washington oils are very similar in their properties, but differ somewhat from the California oils. The New York oils seem to be the most closely related to the foreign oils in all properties, with the exception of the ester content, which is considerably higher. From the standpoint of the increasing ester content the various oils arrange themselves in the following order: Imported, California, Washington, New York, and Oregon, the three latter being very closely related. (See fig. 1.)

No general conclusions can be drawn regarding the possible superiority of any particular oil as compared with any of the other oils. Whether high or low ester content denotes richness or poorness in the quality of the hops, or vice versa, can not be definitely stated. Suffice it to say that from the results obtained it is clear that the geographical source of hops may be indicated by the ester numbers of the oil distilled from the hops, since the experiments show that the ester numbers of the oils from hops of any particular source or season are very similar.

REVIEW OF PREVIOUS CHEMICAL INVESTIGATIONS OF THE AROMATIC CONSTITUENTS OF HOPS

Reference to the odor of hops was made in literature as early as 1819. Loiseleur Deslongchamps (1819) mentioned the cones of hops as possessing a bitter taste and a strong odor resembling garlic. Hanin (1819) reported that the yellow powder of hops was very tasteful, very odorous, and inflammable, with all the characteristics of a resin. Ives (1821) in an investigation of the properties of hops, referred to the yellow powder of the cones as "lupulin," which, he stated, contained the bitter principle and the aromatic flavor of the hops. Working with samples of 1 dram to 2 ounces of lupulin, no volatile oil was separated, but the aqueous distillate possessed the odor of hops. The following year Payen and Chevalier (1822) found that by distilling the yellow powder (lupulin) a volatile oil was obtained which had the characteristic odor of hops.

The first investigation concerning the nature of the oil was made by Wagner (1853) who distilled the oil directly from the hops instead of from the lupulin. The oil was described as being bright brownish yellow in color with a strong odor of hops and a burning, slightly bitter taste. The solubility of the oil in water was sufficient to impart a decided hop odor, the solubility being influenced by dextrin, sugar, hop extract, etc. It was stated that the oil contained a terpene, which was likened to camphene, and also an oxygenated constituent, isomeric with borneo camphor.

According to Personne (1854), lupulin when boiled with water produced a volatile oil and a nonvolatile residue. Valerianic acid was identified among the volatile products; also an oxygenated compound called "valerol." Some years later Kuhne-mann (1877) distilled hops with steam and obtained an oily substance which he called "hop oil." The oil was described as being a mixture of hydrocarbons and oxygenated compounds, the latter consisting of alcohols and acids. Ossipow (1883)

distilled commercial lupulin and obtained an oil. By experimenting with the oxidation of the oil he identified acetic and isovalerianic acids. Octoic, or caprylic, acid was identified in the aqueous distillate from the oil by means of the silver salt. In the aqueous distillate from the lupulin he also identified butyric and valerianic acids (1886).

It was not until 1893 that Chapman (1893) undertook the study of hop oil and obtained some insight regarding its actual composition. He found in his first experiments that an oil which had been standing for 11 months boiled considerably higher than freshly distilled oil and contained a sesquiterpene as its chief constituent. Continuing his work on the composition of the oil, he concluded after careful fractionation that the sesquiterpene which he had found as the chief constituent was humulene (1894; 1895a). The highest boiling fraction (263° to 266° C.), which consisted chiefly of humulene, represented in most cases about 40 per cent of the oil. The lowest boiling fraction (about 170° C.) also represented a large proportion of the oil and was considered to be a terpene hydrocarbon. The middle fractions had a pleasant odor and consisted of oxygenated compounds. The humulene from the highest boiling fraction of the oil was subsequently investigated by Chapman (1895b) and several crystalline derivatives of this compound were prepared. In a later report (1898) he stated that the oil contained no phenols, aldehydes, or ketones; that it was sparingly soluble in water, but sufficiently so to impart a characteristic odor to the water; also that the oil changed in the air to a viscous mass. In 1903 the investigation was continued (Chapman, 1903), and the lowest boiling fraction (166° to 168° C.) was found to have properties similar to myrcene from oil of bay. One of the higher boiling fractions had a strong odor, which fraction, it was stated, probably contained linalool or esters of linalool. The acids obtained by saponification of the oil were identified by means of their silver salts as valerianic and isononic acids. In all freshly distilled samples of the oil, myrcene and humulene were said to be present to the extent of 80 to 90 per cent.

Semmler and Mayer (1911) by the preparation of a number of characteristic derivatives established the identity of the terpene from hop oil with the terpene myrcene.

According to Deussen (1911) the humulene of hop oil is very similar in general properties and crystalline derivatives to the sesquiterpene caryophyllene.

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